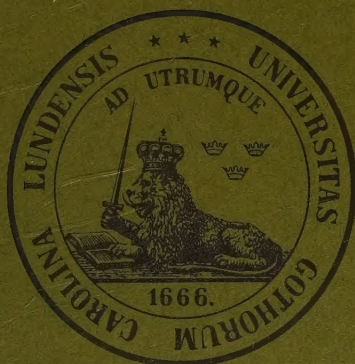


THE COORDINATION OF UNIVALENT THAL- LIUM AND RUBIDIUM IN THE SOLID STATE

A comparative structural study

BENGT BOSSON



LUND 1977

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AVHANDLING FÖR TEKNOLOGIE DOKTORSEXAMEN

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THE COORDINATION OF UNIVALENT THALLIUM AND RUBIDIUM IN THE
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ABSTRACT

The crystal structure of the isotypic compounds $\text{TlZnSO}_4\text{Cl}/\text{RbZnSO}_4\text{Cl}$, $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]/\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and of $\text{Tl}_2\text{S}_2\text{O}_3$ have been determined from three-dimensional X-ray data. In the pairs of isotypic salts the coordination of the Tl^+ ion is compared to that of the Rb^+ ion. The stereochemical activity of the inert electron pair of the Tl^+ ion is discussed. It is concluded that this activity depends on the degree of sp-hybridization of the Tl^+ ion, which varies with different ligands.

The investigated structures are related to other thallium and rubidium salts.

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1. INTRODUCTION

This work forms part of a project dealing with diffraction studies of neutral and basic salts of heavy metals carried out at the Division of Inorganic Chemistry 2, University of Lund. The aim of the actual structural investigations have been to elucidate the coordinations of univalent thallium and rubidium in the solid state.

Thallium(I) and rubidium have almost the same ionic radii and the same valency. They can thus replace each others in solid solutions. However, Tl(I) has an inert electron pair ($6s^2$) in contrast to Rb(I) which could result in differences in the coordination spheres of the ions.

Ion	Electron structure
Tl ⁺	KLMN $5s^2 5p^6 5d^{10} 6s^2$
Rb ⁺	KLM $4s^2 4p^6$

The papers I-III concerning this problem have been published within the aim of the project:

- I. Bosson, B. The Crystal Structure of Tl(ZnSO₄Cl).
Acta Chem. Scand. 27 (1973) 2230.¹
- II. Bosson, B. The Crystal Structures of Tl₃[Hg(SO₄)₂][HgSO₄Cl] and Rb₃[Hg(SO₄)₂][HgSO₄Cl].
Acta Chem. Scand. A30 (1976) 241.²
- III. Bosson, B. The Crystal Structures of RbZnSO₄Cl and TlZnSO₄Cl.
Acta Cryst. B32 (1976) 2044.³

In connection with this work the following study was performed:

- IV. Andersson, J-E. and Bosson, B. Thallium(I)Thiosulphate.
Acta Cryst. B32 (1976) 2225.⁴

A survey of the structural chemistry in the solid state of the Tl^+ and Rb^+ ions is given, where similarities and differences are discussed in view of the coordination spheres around respective ion. The structural disorder of the $\text{S}_2\text{O}_3^{2-}$ ion in $\text{Tl}_2\text{S}_2\text{O}_3$ is also discussed and related to similar disordering in other tetrahedral ions.

2. PREPARATIVE WORK

2.1 Syntheses of TlZnSO_4Cl and RbZnSO_4Cl

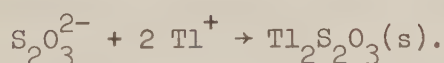
Single crystals of RbZnSO_4Cl and TlZnSO_4Cl were prepared by melting MCl ($\text{M} = \text{Rb}$ or Tl) and anhydrous ZnSO_4 in the molar ratio 1:1 at 440°C in porcelain crucibles.⁵ The samples were cooled $10^\circ/\text{hour}$ until the temperature 200°C was reached. The prepared crystals consisted of colourless, transparent thin plates.

2.2 Syntheses of $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and $\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$

Single crystals of $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and $\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ were prepared by melting MCl , M_2SO_4 ($\text{M} = \text{Tl}$, Rb) and anhydrous HgSO_4 in the molar 1:1:2 in a sealed gold tube at a temperature of 700°C . The crystals were in the form of transparent thin plates.

2.3 Synthesis of $\text{Tl}_2\text{S}_2\text{O}_3$

A hot concentrated solution of sodiumthiosulphate and thallium(I)nitrate were allowed to react according to:⁶



Thallium(I)nitrate must be kept in excess, otherwise TlNaS_2O_3 may be formed. Thin colourless plates of thalliumthiosulphate precipitated during the cooling of the solution.

3. DETERMINATION OF THE STRUCTURES

The structure determination are based on three-dimensional X-ray intensity data. The intensity measurements have been performed with different methods viz. with filmdata, linear and four-circle single-crystal diffractometers depending on the fact that the prevent study has been prolonged during a relative long time.

For further details, see Table 3.1.

Table 3.1. Intensity data collections

Compound	Method	Radiation	No. of recorded reflexions	No. of reflexions used in the final calculations
$\text{TlZnSO}_4\text{Cl}^1$	film	MoK α Zr-filter	656	656
$\text{TlZnSO}_4\text{Cl}^3$	diffraction pailred	MoK α Zr-filter	1716	1230
RbZnSO_4Cl	diffraction CAD 4	CuK α	1127	1031
$\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$	diffraction CAD 4	MoK α	1544	1465
$\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$	diffraction CAD 4	MoK α	2046	1971
$\text{Tl}_2\text{S}_2\text{O}_3$	diffraction CAD 4	MoK α	713	394

Space groups and preliminary cell dimensions were in all cases determined from rotation and Weissenberg photographs. More accurate cell parameters were obtained from least-squares refinements of $\sin^2\theta$ -values taken from Guinier powder diffractograms or from the accurate settings of some reflexions measured on the single-crystal diffractometer. The homogeneity of all the samples were checked by X-ray Guinier-Hägg photographs.

The densities were measured by the displacement method with benzene. Some crystal data are presented in Tables 3.2-3.4.

Table 3.2. Crystal data for TlZnSO_4Cl and RbZnSO_4Cl

Compound	TlZnSO_4Cl	RbZnSO_4Cl
Unit cell	$a = 7.278(1) \text{ \AA}$ $b = 9.551(1) \text{ \AA}$ $c = 8.092(1) \text{ \AA}$ $\beta = 93.97(1)^\circ$ $V = 561.0(2) \text{ \AA}^3$ $Z = 4$	$a = 7.2610(3) \text{ \AA}$ $b = 9.6152(5) \text{ \AA}$ $c = 8.3086(6) \text{ \AA}$ $\beta = 95.542(6)^\circ$ $V = 577.42(6) \text{ \AA}^3$ $Z = 4$
Formula weight	$M = 401.3$	$M = 282.4$
Density 20°C	$D_m = 4.90 \text{ g}\cdot\text{cm}^{-3}$ $D_x = 4.75 \text{ g}\cdot\text{cm}^{-3}$	$D_m = 3.37 \text{ g}\cdot\text{cm}^{-3}$ $D_x = 3.25 \text{ g}\cdot\text{cm}^{-3}$
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Linear absorption coefficient	$\mu(\text{MoK}\alpha) = 340 \text{ cm}^{-1}$	$\mu(\text{CuK}\alpha) = 247 \text{ cm}^{-1}$

Table 3.3. Crystal data for $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and $\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$

Compound	$\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$	$\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$
Unit cell	$a = 7.870(1) \text{ \AA}$ $b = 9.752(1) \text{ \AA}$ $c = 9.945(1) \text{ \AA}$ $\beta = 110.72(1)^\circ$ $V = 713.9(1) \text{ \AA}^3$ $Z = 2$	$a = 7.862(2) \text{ \AA}$ $b = 9.790(4) \text{ \AA}$ $c = 10.002(1) \text{ \AA}$ $\beta = 111.12(2)^\circ$ $V = 718.0(4) \text{ \AA}^3$ $Z = 2$
Formula weight	$M = 1337.9$	$M = 981.2$
Density 20°C	$D_m = 6.22 \text{ g}\cdot\text{cm}^{-3}$ $D_x = 6.10 \text{ g}\cdot\text{cm}^{-3}$	$D_m = 4.45 \text{ g}\cdot\text{cm}^{-3}$ $D_x = 4.48 \text{ g}\cdot\text{cm}^{-3}$
Space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
Linear absorption coefficient	$\mu(\text{MoK}\alpha) = 565 \text{ cm}^{-1}$	$\mu(\text{MoK}\alpha) = 334 \text{ cm}^{-1}$

Table 3.4. Crystal data for $\text{Tl}_2\text{S}_2\text{O}_3$

Compound	$\text{Tl}_2\text{S}_2\text{O}_3$
Unit cell	$a = 8.433(7) \text{ \AA}$ $b = 6.184(3) \text{ \AA}$ $c = 10.911(3) \text{ \AA}$ $V = 569.01 \text{ \AA}^3$ $Z = 4$
Formula weight	$M = 520.9$
Density 20°C	$D_m = 6.21 \text{ g}\cdot\text{cm}^{-3}$ $D_x = 6.10 \text{ g}\cdot\text{cm}^{-3}$
Space group	Pnma (No. 62)
Linear absorption coefficient	$\mu(\text{MoK}\alpha) = 578 \text{ cm}^{-1}$

The intensity data were all corrected for Lorentz, polarization and absorption effects. For TlZnSO_4Cl (film data) and RbZnSO_4Cl corrections for secondary extinction were applied. The results were not improved, however.

In TlZnSO_4Cl the coordinates of the thallium atom were obtained from a three-dimensional Patterson function. The other atoms were located from three-dimensional electron density difference syntheses. The positional parameters of the atoms in the thallium compound were used as preliminary parameters for the rubidium salt.

At the structure determination of $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ the positions of the heavy metal atoms were found from a combination of a three-dimensional Patterson function and direct methods. The chlorine, sulfur and oxygen atoms were located from a three-dimensional electron density difference synthesis. The atomic parameters for the thallium salt were used as preliminary parameters for the rubidium salt.

Preliminary positions of the atoms in $\text{Tl}_2\text{S}_2\text{O}_3$ were taken from the isostructural compound K_2SO_4 .⁷ The least-squares refinements of the structures of the above-mentioned salts, except $\text{Tl}_2\text{S}_2\text{O}_3$ were performed in the usual way.¹⁻³ In the least-squares refinement of the atomic parameters of $\text{Tl}_2\text{S}_2\text{O}_3$ the sulphur atom of one of the corners of the thiosulphate tetrahedron was assumed to be distributed into two different crystallographic positions. It was not possible to separate this sulphur atom from two oxygen atoms in the tetrahedron, however.

The atomic scattering factors used in the calculations were taken from International Tables,⁸ Cromer et al.,^{9,10} and Doyle et al.¹¹ The scattering factors for Tl and Hg were corrected for anomalous dispersion.

4. SHORT DESCRIPTIONS OF THE DETERMINED STRUCTURES

4.1 TlZnSO_4Cl and RbZnSO_4Cl

The crystal structures of TlZnSO_4Cl and RbZnSO_4Cl are built up of infinite layers of the composition $[\text{ZnSO}_4\text{Cl}]_n^{n-}$ parallel to (100). From a geometrical point of view the sheets can be described as being built up of sulphate tetrahedra and " ZnO_3Cl tetrahedra" as each zinc atom is coordinated to one chlorine and three oxygen atoms, belonging to three different sulphate groups. Every " ZnO_3Cl tetrahedron" is thus linked by sharing three corners to sulphate tetrahedra. Each of the sulphate tetrahedra is linked to three " ZnO_3Cl tetrahedra", cf. Fig. 4.1. The sheets $[\text{ZnSO}_4\text{Cl}]_n^{n-}$ are held together by Tl^+ or Rb^+ ions.

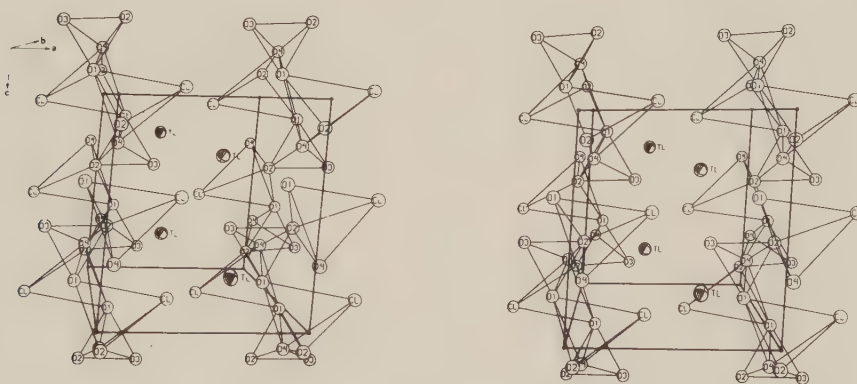


Fig. 4.1. A stereoscopic pair of drawings showing the infinite layers $[\text{ZnSO}_4\text{Cl}]_n^{n-}$ parallel to (100) and the Tl^+ ions in the crystal structure of TlZnSO_4Cl . The small tetrahedra denote the sulphate groups and the larger ones the " ZnO_3Cl tetrahedra".

The coordination of the thallium and rubidium ions are very similar. The polyhedron may be described as a distorted three-capped trigonal prism, with the cation surrounded by three chlorine and six oxygen atoms. Distances are given in Table 4.1.

Table 4.1. The closest neighbours of the cations in TlZnSO_4Cl and RbZnSO_4Cl . The distances are given in Å.

Compound	TlZnSO_4Cl	Compound	RbZnSO_4Cl
Tl-O(3)	2.89(1)	Rb-O(3)	2.90(1)
-O(3)	3.01(1)	-O(3)	2.94(1)
-O(4)	3.18(1)	-O(4)	3.04(1)
-O(1)	3.24(1)	-O(1)	3.11(1)
-O(2)	3.16(1)	-O(2)	3.11(1)
-Cl	3.206(4)	-Cl	3.334(3)
-Cl	3.275(3)	-Cl	3.342(3)
-Cl	3.293(4)	-Cl	3.396(3)
-O(3)	3.48(1)	-O(3)	3.69(1)

4.2. $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and $\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$

The structures of $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and the isotypic rubidium salt are mainly ionic crystals. Discrete ions $\text{Hg}(\text{SO}_4)_2^{2-}$, HgSO_4Cl^- and Tl^+ or Rb^+ constitute the two substances.

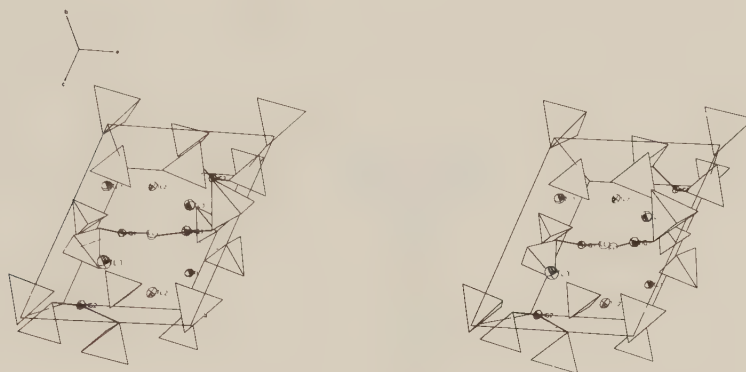


Fig. 4.2.1. A stereoscopic pair of drawings showing the ions $\text{Hg}(\text{SO}_4)_2^{2-}$, HgSO_4Cl^- and Tl^+ . The tetrahedra denote the sulfate groups.

In the structure (Fig. 4.2.1) there are two kinds of mercury atoms, denoted Hg(1) and Hg(2). The Hg(1) atom has two close ligands, one oxygen atom and one chlorine atom viz. in a nearly linear geometry. In this way a HgSO_4Cl^- ion is formed. Three additional oxygen atoms from three other sulfate tetrahedra complete the distorted trigonal bipyramid around Hg(1).

The mercury atom Hg(2) is bonded to two oxygen atoms from different sulfate groups, none of which is linking further mercury atoms. In this way a $\text{Hg}(\text{SO}_4)_2^{2-}$ ion is formed. Three additional oxygen atoms are situated at somewhat larger distances from the mercury atom. The polyhedron of Hg(2) is also a distorted trigonal bipyramid.

In the paper ² is stated that discrete mercury complexes in the solid

state only is reported for the structure of $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$.^{12,13} Recently the structure of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ ^{14,15} has been refined (neutron single-crystal data) giving as result the structure contains discrete mercury complexes, $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ (Fig. 4.2.2).

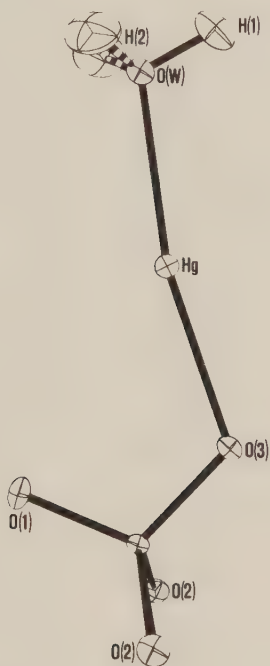


Fig. 4.2.2. The discrete $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ molecule in the structure of mercury(II) sulphate monohydrate. The hydrogen atom H(2) of the water molecule is disordered.

In the structures there are three different thallium respectively rubidium ions, all irregularly surrounded by oxygen and chlorine atoms. The distances are given in Table 4.2.

Table 4.2. Distances (Å) between cations and surrounding atoms in

 $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and $\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$

Distances	M = Tl	M = Rb
M(1)-O	2.80(3)	2.91(2)
M(1)-O	2.90(3)	2.97(2)
M(1)-O	2.96(3)	2.91(2)
M(1)-O	3.03(4)	3.08(3)
M(1)-O	3.03(3)	3.02(2)
M(1)-O	3.08(3)	3.05(2)
M(1)-O	3.14(4)	2.96(2)
M(1)-O	3.25(3)	3.43(2)
M(1)-Cl	3.35(1)	3.38(1)
M(1)-O	3.45(4)	3.39(3)
M(2)-O	2.60(4)	2.81(2)
M(2)-O	2.87(3)	3.06(2)
M(2)-O	2.94(4)	3.00(3)
M(2)-O	3.00(4)	2.86(3)
M(2)-O	3.09(3)	3.05(2)
M(2)-O	3.14(4)	3.03(2)
M(2)-O	3.21(4)	3.16(2)
M(2)-Cl	3.34(1)	3.32(1)
M(2)-O	3.40(3)	3.24(2)
M(3)-O	2.68(4)	2.78(3)
M(3)-O	2.89(3)	2.96(2)
M(3)-O	2.95(4)	2.87(2)
M(3)-O	3.16(4)	3.20(2)
M(3)-O	3.20(3)	3.30(2)
M(3)-O	3.44(4)	3.36(2)
M(3)-O	3.54(3)	3.52(2)
M(3)-O	3.53(3)	3.49(2)
M(3)-O	3.55(3)	3.38(2)
M(3)-Cl	3.60(1)	3.66(1)

4.3. $\text{Tl}_2\text{S}_2\text{O}_3$

The structure of $\text{Tl}_2\text{S}_2\text{O}_3$ is built up of $\text{S}_2\text{O}_3^{2-}$ and Tl^+ ions. The tetrahedral $\text{S}_2\text{O}_3^{2-}$ ion takes various positions around the O(1)-S(1) line in the tetrahedron (Fig. 4.3.1).

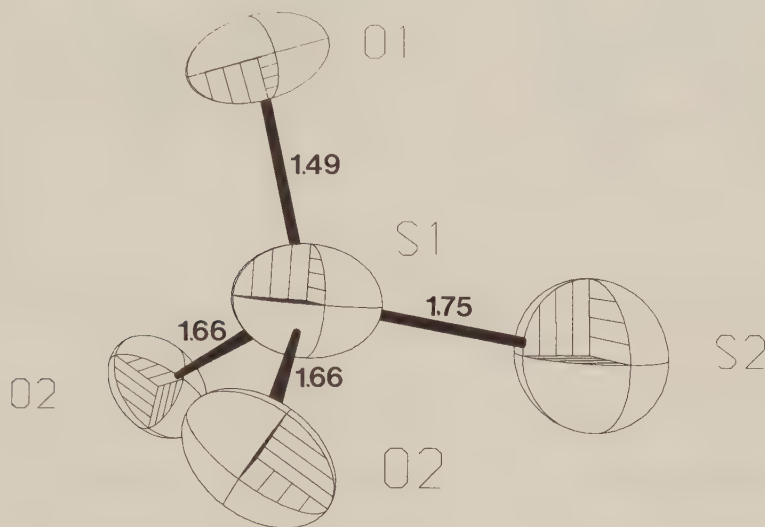


Fig. 4.3.1. Perspective drawing showing the distances (Å) within the $\text{S}_2\text{O}_3^{2-}$ group. The thermal ellipsoids are drawn with 90 % probability.

Due to this stepwise rotation S(2) and the two O(2) atoms cannot clearly be distinguished. About 50 % sulphur and 50 % oxygen are situated in the position S(2), which causes an occupation of about 25 % sulphur and 75 % oxygen in the O(2) positions.

The fact that the structure is partly disordered makes it difficult to discuss the environments of the two thallium atoms. Tl(1) is coordinated to two oxygen atoms, not statistically distributed, at the identical distances of 3.15 Å; further surrounded by five sulphur or oxygen atoms ranging from 3.07 to 3.22 Å. These seven atoms are bonded to Tl(1) one-sidedly.

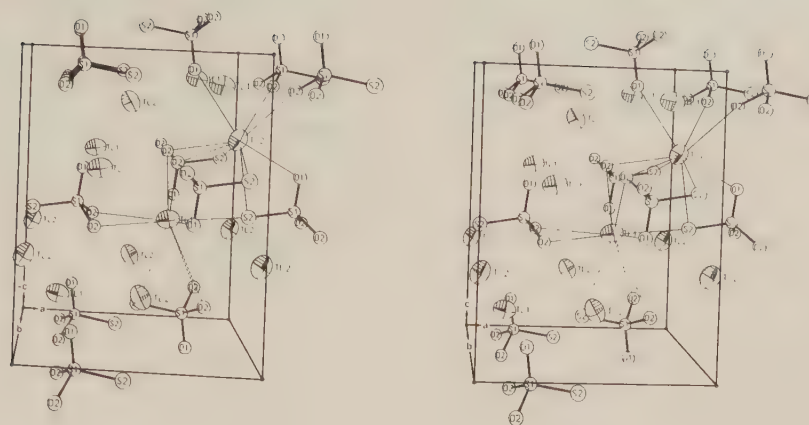


Fig. 4.3.2. A stereo view of the structure of $\text{Tl}_2\text{S}_2\text{O}_3$.

In addition, three oxygen or sulphur atoms are situated at approximately 3.46 Å (cf. dashed lines in Fig. 4.3.2). These atoms have only weak interactions with the thallium atom, which may be one of the reasons for the $\text{S}_2\text{O}_3^{2-}$ groups being partly disordered. As Tl(1) does not coordinate these more distant atoms, a cavity is formed in the structure.

Tl(2) is irregularly surrounded by nine atoms, viz. two oxygen at the distances 2.91 and 3.06 Å and seven sulphur or oxygen atoms ranging from 3.11 to 3.29 Å, cf. Table 4.3.1.

Table 4.3.1. Selected distances (Å) in $\text{Tl}_2\text{S}_2\text{O}_3$. Remark, in the position denoted O(2) are situated about 75 % oxygen and 25 % sulphur and in S(2) about 50 % sulphur and 50 % oxygen.

Compound	$\text{Tl}_2\text{S}_2\text{O}_3$
Tl(1)-O(2) x 2	3.07(2)
-S(2)	3.12(2)
-O(1) x 2	3.15(1)
-O(2) x 2	3.22(2)
-O(2) x 2	3.46(2)
-S(2)	3.47(1)
Tl(2)-O(1)	2.91(3)
-O(1)	3.06(3)
-O(2) x 2	3.11(2)
-O(2) x 2	3.16(2)
-S(2)	3.20(2)
-S(2) x 2	3.29(1)

Table 4.3.2. A survey of distances (Å) between the cations and the ligand atoms of the tetrahedral ions in some compounds.

Atoms	$\text{Tl}_2\text{S}_2\text{O}_3$ ⁴	Rb_2SO_4 ¹⁸	Tl_2SO_4 ¹⁹	Rb_2CrO_4 ²⁰	Tl_2CrO_4 ²¹
Rb(1) or Tl(1)-O(2)/O3(2x)	3.07(2x)	3.05(2x)	3.03(2x)	3.11(2x)	2.98(2x)
-S(2)/O1	3.12	2.91	2.99	3.06	2.70
-O(1)/O2	3.15(2x)	3.02(2x)	3.00(2x)	3.16(2x)	2.98(2x)
-O(2)/O3	3.22(2x)	3.16(2x)	3.17(2x)	3.17(2x)	3.36(2x)
-O(2)/O3	3.46(2x)	3.20(2x)	3.26(2x)	3.35(2x)	3.31(2x)
-S(2)/O1	3.47	3.52	3.64	3.66	3.79
-O(1)/O2	3.78	>4.0	3.18	3.20	3.52
Rb(2) or Tl(2)-O(1)/O2	2.91	2.88	2.96	3.05	2.71
-O(1)/O2	3.06	2.95	3.09	2.86	2.85
-O(2)/O3	3.11(2x)	2.89(2x)	2.85(2x)	2.86(2x)	2.80(2x)
-O(2)/O3	3.16(2x)	2.96(2x)	2.98(2x)	3.07(2x)	2.82(2x)
-S(2)/O1	3.20	3.05	2.97	3.11	3.09
-S(2)/O1	3.29(2x)	3.24(2x)	3.21(2x)	3.41(2x)	3.23(2x)

A comparison with some isostructural compounds reveals no apparent differences in the environments of the corresponding cations (Table 4.3.2). This indicates that the Tl^+ in $\text{Tl}_2\text{S}_2\text{O}_3$ may not be stereochemically active. The environments of the Rb^+ ions in the isostructural compound Rb_2SO_4 is given in Fig. 4.3.3.

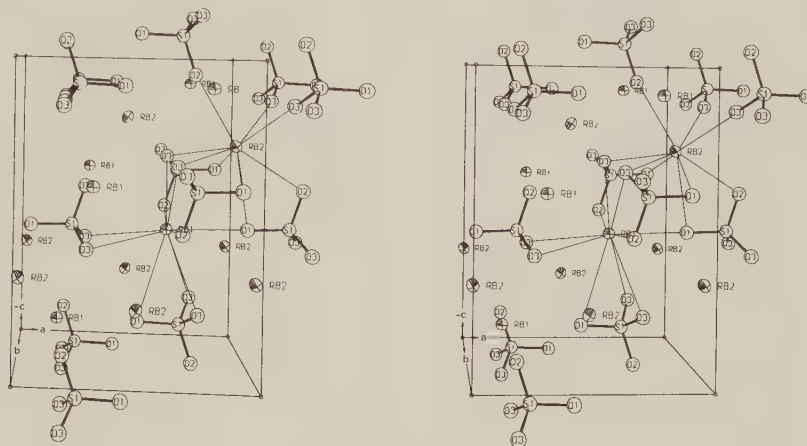


Fig. 4.3.3. A stereo view of the structure of Rb_2SO_4 .

A similar disordering as indicated for the $\text{S}_2\text{O}_3^{2-}$ ion in $\text{Tl}_2\text{S}_2\text{O}_3$ has also been observed for the CrO_3F^- ion in KCrO_3F ¹⁶, where this ion forms an almost regular tetrahedron. The random orientation of CrO_3F^- is explained by the similar size of the oxide and fluoride ions. The CrO_3Cl^- ion, in the structure of KCrO_3Cl ¹⁶, is distorted and not disordered. This ion would be more comparable with the $\text{S}_2\text{O}_3^{2-}$ ion because the sizes of chlorine and sulphur atoms are about the same. Neither in RbCrO_3Cl ¹⁷ nor in CsCrO_3Cl ¹⁷ there are any random orientations of the tetrahedral anions.

5. IONIC BONDING DISTANCES OF RUBIDIUM AND UNIVALENT THALLIUM

The reason why rubidium has been chosen to replace univalent thallium in the structures dealt with in this abstract, is that both of them are univalent and have about same ionic radii. Table 5.1 gives ionic radii of interest for the following discussion.

Table 5.1. Values of ionic radii (Å) according to different authors.

Ion	Goldschmidt ²²	Pauling ²³	Ladd ²⁴	Shannon and Prewitt ^{25,26}
Rb ⁺	1.49	1.48	1.58	1.52
Tl ⁺	1.49	1.40	1.54	1.50
F ⁻	1.33	1.36	1.19	1.33
Cl ⁻	1.81	1.81	1.70	1.80
Br ⁻	1.96	1.95	1.87	1.95
I ⁻	2.20	2.16	2.12	2.15
O ²⁻	1.32	1.40	1.25	1.40
S ²⁻	1.74	1.84	1.70	1.85

The values of the ionic radii given in Table 5.1 are relevant only for six-coordination. When the interatomic distances and hence the ionic radii increase, giving a larger coordination number²⁸, it is necessary to work with an ionic distance for every specific case. It is worth noticing that the change in anion radii is smaller than in cation radii²⁵. Since the radius of an ion depends on its coordination number it is usual to adopt the number six as standard. If the radius of a cation is given the value 1.00 the following relative values for different coordination numbers can be used in calculations:

Coord. number	12	9	8	6	5	4	3	2	1
Rel. radii	1.09	1.05	1.04	1.00	0.98	0.95	0.92	0.87	0.80

23

Goldschmidt derived a set of radii to be used only for ionic crystals. These radii were obtained from average interatomic distances M-O and M-F (M = metal ion) using $r(O^{2-}) = 1.32 \text{ \AA}$ and $r(F^-) = 1.33 \text{ \AA}$. Pauling calculated a set of values, with respect to the variation in the effective nuclear charge, assuming $r(O^{2-}) = 1.40 \text{ \AA}$ and $r(F^-) = 1.36 \text{ \AA}$. The ionic radii of Goldschmidt and Pauling are obtained by using the rock-salt type of structure as standard.

The values given by Ladd are determined from a combination of deduced radii and electron density calculations; the radii in good agreement with the experimental results for the free energy of hydration of gaseous ions. Due to the method of deriving, these values should be considered as the most valid ones from a physical point of view.

The set of radii according to Shannon & Prewitt takes into consideration both coordination number and electronic spin state of the first row transition metal ions ($_{21}\text{Sc}-_{29}\text{Cu}$). The term "effective" ionic radii is used to emphasize the fact that these values are empirical. They are calculated from fluoride and oxide structures and are admittedly applicable only to this type of compounds. The radii of both cations and anions vary with the coordination number. Fumi & Tosi²⁷ have defined crystal radii based on $r(O^{2-}) = 1.26 \text{ \AA}$ and $r(F^-) = 1.19 \text{ \AA}$ for six-coordination. If these ionic radii are used nearly the same "effective" ionic bonding distances as given by Shannon & Prewitt are obtained. According to Fumi & Tosi the cations are somewhat larger and the anion somewhat smaller as compared to Shannon & Prewitt.

The variations of the cation radii with different coordination numbers given above are not valid for the values given by Shannon & Prewitt.

Concerning the Rb^+ and Tl^+ ions, cf. Fig. 5.1. As can be seen the increases of the rubidium and thallium ionic radii are fairly parallel when going from coordination number six to twelve. Using this plot, we may assume that the difference in ionic radii between Rb^+ and Tl^+ is throughout 0.02 Å. The variations of the radii of O^{2-} and F^- with the coordination number is given in Table 5.2.

Table 5.2. The ionic radii (Å) of O^{2-} and F^- and their variations with the coordination number (CN).

CN	O^{2-}	F^-
2	1.35	1.285
3	1.36	1.29
4	1.38	1.31
6	1.40	1.33
8	1.42	

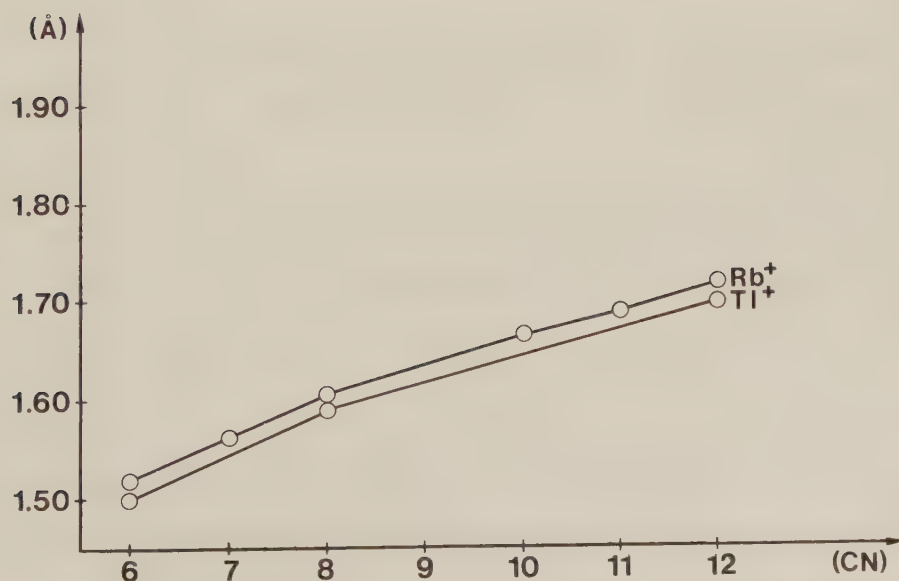


Fig. 5.1. The effective ionic radii (Å) of Rb^+ and Tl^+ as functions of the coordination number (CN) according to Shannon and Prewitt.^{25,26}

6. BOND DISTANCES

6.1. Thallium(I) and Rubidium to halogens

The thallium(I)halides were among the first compounds of thallium to be prepared. Both TlCl and TlBr have a cubic, CsCl-type structure²⁹, while TlF has a distorted NaCl structure³⁰. A high-pressure phase of TlF exists³¹. TlCl and TlBr exhibit no phase transitions with increasing pressure, since the CsCl-structure represents the most stable dense configuration for ionic crystals with this ratio of the ionic radii. It is possible to make them grow from vapour phase on a suitable matrix having the NaCl structure³². The distortion from octahedral symmetry is evident in the room-temperature modification of TlI, which crystallizes with orthorhombic symmetry and has a layer structure in which Tl^+ has five nearest I^- neighbours and two I^- at a larger distance³³, cf. Table 6.1.1. and Fig. 6.1.1.

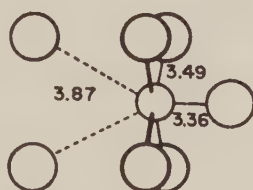


Fig. 6.1.1. Environment of the Tl ion in TlI according to Dunitz and Orgel.³⁴ Distances are given in Angstrom units.

In the TlI-type of structure, about seventy compounds crystallize³⁵. Its relationship to the structures of SrBr_2 and YOOH has recently been confirmed³⁶.

On heating TlI at atmospheric pressure to 170 °C, it is transformed from the orthorhombic structure to a cubic CsCl-structure³³. This transformation of TlI is somewhat anomalous as the high-temperature red phase has the higher density. For a given substance, the phase of lowest density is generally the one of highest entropy and lowest symmetry and would be

expected to be the most stable one at higher temperatures.

At room temperature the rubidium halides crystallize with NaCl-structure.

At elevated pressures the more dense CsCl-structure^{29,37} is formed.

TlF was originally studied by Ketelaar³⁰. The structure was reported to be of the NaCl-type but distorted. It has recently been refined by Alcock³⁸, who describes the structure as being an example of a distortion caused by the inert electron pair of thallium. The two independent Tl^+ ions have different environments, both surrounded by a distorted octahedron of F^- ions of which two are much more distant than the others. This can be seen as the result of an aspherical thallium ion, in which the s^2 lone pair has been distorted, probably by mixing with a p-orbital. When we are talking about an "inert" pair distortion in this connection, we must be aware that we mean a mixing between s- and p-orbitals. The result of the aspherical charge distribution of the Tl^+ ion is that its electron cloud produces a bulge on one side towards the more distant F^- ions (3.07-3.91 Å), and a reduction in size on the other towards the nearest F^- ions (2.25-2.62 Å).

The thallium(I)halides which are not isostructural to the corresponding rubidium halides are TlF and TlI. These phenomena have been explained in terms of s-p mixing on thallium^{34,39}. An antisymmetric displacement of anions from an octahedral or cubic field will lead to mixing of s and p levels and the stabilization due to such mixing will offset the normal forces which hold the octahedron or cube in its regular configuration. If the stabilization is caused by electrostatic forces, it is expected to be greater for the fluorine compound, if it is due to covalent effects, it would be expected to be greatest for the compound of heavier halogens.

We regard the deformation of the Tl^+ ion as an "ionic" s-p hybridization when the ligands are small and strongly electronegative, e.g. F^- (and O^{2-} , cf. below). The deformation disappears for somewhat larger and less electronegative ligands, e.g. Cl^- and Br^- and returns for I^- (and S^{2-}) depending on a more covalent hybridization of the thallium(I) atom.

A measure of the s-p mixing on thallium in the actual compounds can be obtained from magnetic-susceptibility measurements. Thus it has been estimated that in the yellow, orthorhombic form of TlI , the s-p mixing is about 71 % complete on thallium, whereas in the red, cubic form, it is only about 28 % complete⁴⁰. By magnetic-susceptibility measurements it is thus possible to estimate in what extent the "inert" pair is stereochemically active.

In the solid state Tl^+ and Rb^+ have nearly the same ionic radii (Fig. 5.1) which causes the distances Tl-X and Rb-X (X = halides) are about the same, Tl-X somewhat smaller, however, than the corresponding Rb-X distances (Table 6.1.1). This may depend on a higher degree of covalency in the Tl-X bonds. Estimates of these effects in the Tl-X bonds of the cubic forms of TlCl , TlBr and TlI have been made from n.m.r. measurements, giving values of 4, 6 and 10 % for the Tl-Cl , Tl-Br and Tl-I bonds respectively⁴¹.

The covalent contribution of the bondings in univalent thallium substances have, from a more qualitative point of view, been estimated by Shannon & Gurnerman⁴². The effect of covalency on Tl-X bonds can be seen by a

comparison with the more ionic Rb-X bonds. The ratio of the unit cell volumes $R_v = \frac{v(\text{Tl}_m \text{X}_n)}{v(\text{Rb}_m \text{X}_n)}$ are calculated for isotypic compounds with

different anions, where $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ and O . The condition the bonds Tl-X being more covalent than Rb-X implies that the electronegativity (denoted χ) of Tl^+ is greater than that of Rb^+ . In order to see the effect of covalency on the Tl-X bonds relative to the Rb-X bonds, Shannon & Gummerman have plotted R_v vs $\Delta\chi_{\text{Tl-X}}$ (Fig. 6.1.2).

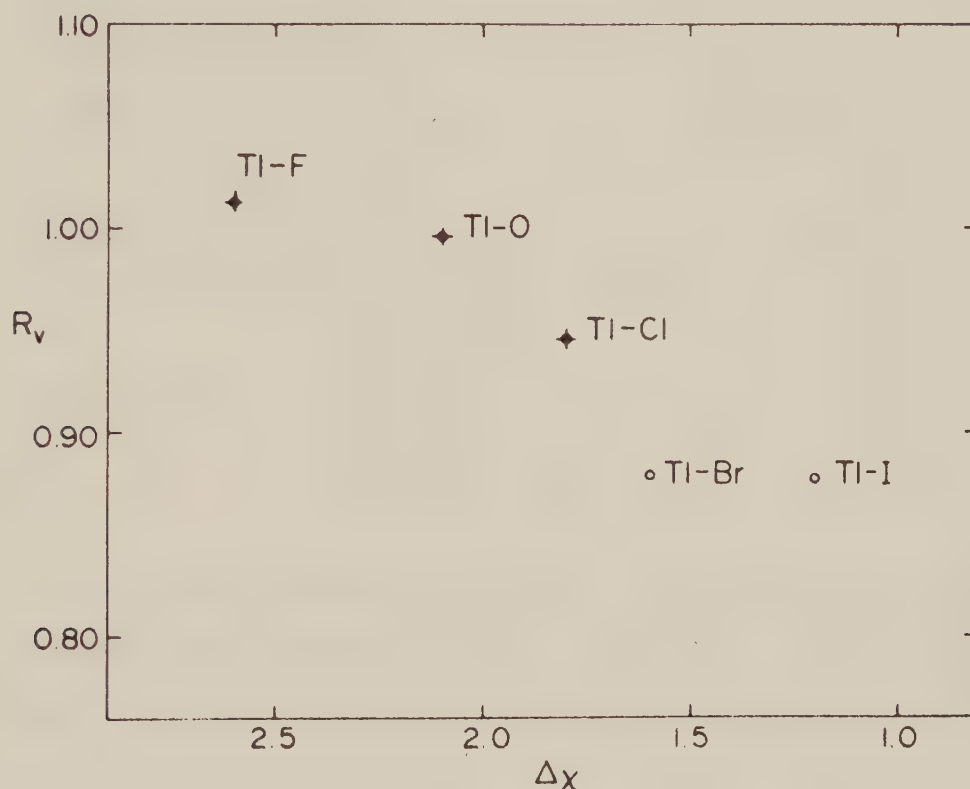


Fig. 6.1.2. The ratio of the cell volumes R_v as functions of $\Delta\chi$ according to Shannon and Gummerman.⁴²

As can be seen in Fig. 6.1.2. R_v is a diminishing function of decreasing $\Delta\chi_{\text{Tl-X}}$. The decrease in Tl-X distances relative to Rb-X is, at least partly, attributed to an increase in covalent character of the Tl-X bonds as $\Delta\chi_{\text{Tl-X}}$ decreases. The same phenomena may perhaps be explained, in another way, if we assume that the "ionic" s-p hybridization increases as the ligands become more electronegative, cf. Andersson & Åström^{43,44} who have shown that the inert electron pairs in some oxides or oxide fluorides require a space comparable with that of an anion. Furthermore

there is a clear empirical correlation (Table 6.1.2.) between the elements with stable s^2 ions, Tl^+ , Sn^{2+} and Pb^{2+} , where a small anion gives a distorted structure and a large one a regular structure. Also, the smaller the cation is, the larger is the anion needed to produce a regular structure.

Table 6.1.2. Distorted and undistorted MX structures (anion size increased from left to right) according to Alcock.³⁸

Distorted	Undistorted
TlF	$TlCl$, $TlBr$
SnO , SnS , $SnSe$	$SnSe$, $SnTe$
PbO	PbS , $PbSe$, $PbTe$

If we complete Table 6.1.2. for the thallium(I) atom by adding Tl_2O , Tl_2S and TlI (orthorombic) to the distorted structures then the table is not only valid for small anions. As has been pointed out earlier we obtain a distorted structure even for larger and less electronegative anions caused by a covalent hybridization of the thallium(I) atom.

A comparison between the shortest distances $Tl-X$ and $Rb-X$ ($X = F, Cl, Br, I$) respectively, for the compounds given in Table 6.1.1, shows the greatest difference 0.43 Å for the fluorides, where the $Tl-F$ distance is 2.25 Å and $Rb-F$ 2.68 Å. As the structure determination of Rb_2BeF_4 , giving the $Rb-F$ distance 2.61 Å seems to be rather uncertain ($R(h0l) = 0.13$; $R(0kl) = 0.09$) the $Rb-F$ distance 2.68 reported for $RbTlF_4$ was used. The differences between the shortest $Tl-X$ and $Rb-X$ distances are 0.14 Å for both the chlorides and bromides. Furthermore the difference increases to 0.27 Å for the iodides.

Table 6.1.1. Coordination number, structure type (or coordination polyhedron) and bond distances for some thallium(I) and rubidium halides.

Compound	Coord. number	Structure type	Distances (Å) Tl-X and Rb-X	Remarks	Ref.
TlF	6 6	octahedron, distorted	2.54-3.50 2.25-3.91	stereochemical active electron pair	38
TlBe ₂ F ₅	6	octahedron, distorted	2.69-3.25	isotypic to RbBe ₂ F ₅	45
TlCl	6	NaCl	3.15		32
TlCl	8	CsCl	3.32		29
Tl(I)Tl(III)Cl ₄	8	cube, distorted	3.27(4x), 3.29(4x)		46
TlBr	6	NaCl	3.29		32
TlBr	8	CsCl	3.44		29
Tl(I)Tl(III)Br ₄	8	dodecahedron, irregular	3.46(mean value)		47
Tl ₄ HgBr ₆	8	irregular	3.29-3.70		48
TlI	6	NaCl	3.47		32
TlI	8	CsCl	3.64	light red form	29
TlI	5+2	layer structure	3.36, 3.49(4x), 3.87(2x)	yellow form	33
RbF	6	NaCl	2.82		29
RbF	8	CsCl	2.83	high pressure form	37
RbBF ₄	5		2.92-3.05		49
RbTlF ₄	10	irregular	2.68-3.45		50
RbBe ₂ F ₅	8	octahedron, distorted	2.82-3.08		51
Rb ₂ BeF ₄	6	octahedron, distorted	2.87-3.05	isotypic to TlBe ₂ F ₅	52
	8		2.61-2.96		
RbPaF ₆	10	irregular	2.81-3.17		53
Rb ₂ CrF ₅	10	irregular	2.83-3.09		54
	10	"	2.89-3.19		
RbLi ₂ Be ₂ F ₇	7	irregular	2.93-3.11		55
Rb ₂ NaErF ₆	12	irregular	3.14(12x)		56
RbCl	6	NaCl	3.29		29
RbCl	8	CsCl	3.36	high pressure form	37
RbMgCl ₃	12	cube octahedron	3.54(6x), 3.67(6x)		57
	12	" "	3.60(6x), 3.55(6x)		
RbBr	6	NaCl	3.43		29
RbI	6	NaCl	3.67		29
RbI	8	CsCl	3.72	high pressure form	29
RbAg ₄ I ₅	6	octahedron	3.63		58

6.2. Thallium(I) and Rubidium to oxygen

There are two well-defined oxides containing univalent thallium, viz. Tl_2O and the mixed oxide Tl_4O_3 . In the structure of Tl_2O sheets of edge- and corner sharing tetrahedra appear. One of the corners in the tetrahedron is assumed to be occupied by a lone pair of electrons (Fig. 6.2.1). The compound Cs_2O adopts the same structure, probably depending on a polarization of the large Cs^+ ion.

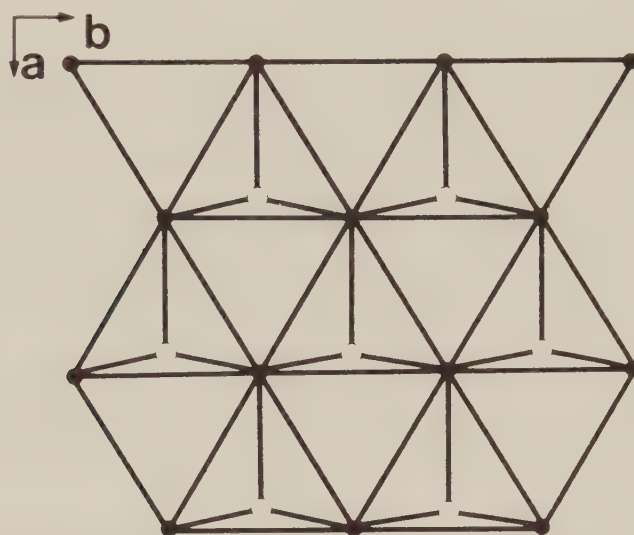


Fig. 6.2.1. The sheet of tetrahedra formed in the structure of Tl_2O , projected along the c-axis, the drawing according to Bovin.⁵⁹ Small filled circles indicate oxygen atoms and large open ones lone pairs.

This coordination polyhedron is common in connection with stereochemical active thallium(I) substances. From values of the s-p mixing (cf. TlI , orth) in different compounds, where the hybridization may vary between zero and one hundred percent, the conclusion may be drawn that the stereochemical influence of the inert pair of electrons will vary between absence and full activity. This behaviour of Tl^+ in the solid state is thus connected with different degrees of s-p hybridization. In the same way Sb^{3+} has a full hybridization in most of its salts, on

the other hand the hybridization in salts of the heavier Tl^+ , Pb^{2+} and Bi^{3+} ions vary.

According to the theory given by Gillespie⁶⁰ the lone pair of electrons, requiring larger space than the bonded pairs, press the bonding electrons together which results in distortions from the regular configurations around the ns^2 -elements.

The following three coordination polyhedra are common in oxygen compounds of metals with stereochemically active lone pairs:

1. A tetrahedron with the lone pair at one of the corners.
2. A trigonal bipyramid with the lone pair at one of the equatorial corners.
3. A square pyramid with the lone pair at its apex.

Concerning univalent thallium only the two coordination polyhedra 1, 2 are known at present. Below is given a drawing which illustrates the position of the inert pair in the tetrahedron and the trigonal bipyramid.

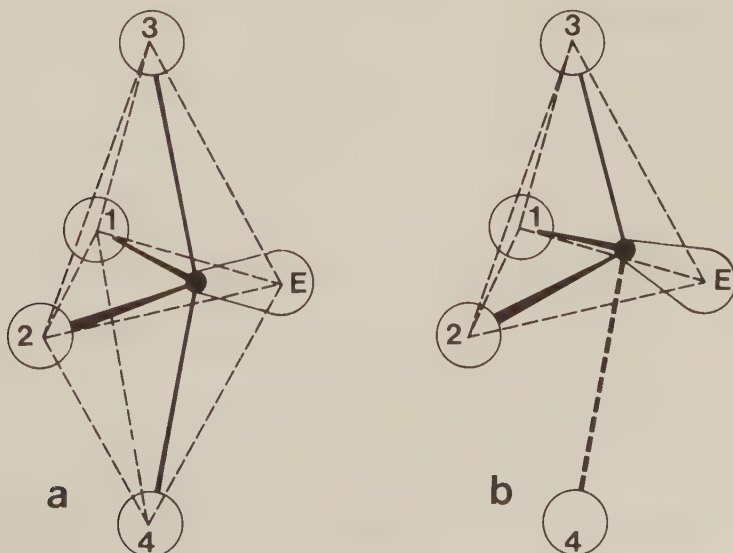


Fig. 6.2.2 Trigonal bipyramidal and tetrahedral coordination polyhedra according to Bovin.⁶¹ E denotes the lone pair and 1-4 ligand atoms.

The thallium oxide Tl_4O_3 is a mixed oxide of Tl(I) and Tl(III) . In this structure the three univalent thallium ions are stereochemically active. One of them has an one-sided coordination and the coordination polyhedra of the other two are triangular pyramids.

Among the rubidium oxides only the structure of Rb_2O is known, which crystallizes in an anti- CaF_2 structure where the rubidium ion is tetrahedrally surrounded by four oxygen atoms.

The tendency of the univalent thallium ion to make use of its inert pair of electrons in a stereochemical active way in its coordination of oxygen atoms, seems, in some extent, to depend on the supply of the latter⁶². Thallium salts, which are rich in oxygen atoms, are often isotypic with corresponding potassium or rubidium salts. On the other hand the inert pair of electrons has a great stereochemical importance in substances with a small supply of oxygen atoms. In salts where the ratio $\frac{O}{\text{Tl(I)}}$ is less than 1.5, the thallium ion has a "non-spherical" charge distribution (Table 6.2.1). At the quotient $\frac{O}{\text{Tl(I)}} = 2$, e.g. in Tl_2SO_4 and Tl_2CrO_4 , the ns^2 electrons of thallium are not stereochemically active. In the substances TlVO_3 and TlSbO_3 ($\frac{O}{\text{Tl}} = 3$) only the last-mentioned compound shows a stereochemically active pair of electrons. The conclusion which can be drawn from Table 6.2.1. is, that with a ratio $\frac{O}{\text{Tl(I)}} \leq 1.5$ thallium has an one-sided coordination. The ratios $\frac{O}{\text{Tl(I)}}$ discussed above are only valid if all the oxygen atoms are able to be bonded to the thallium ion. In the structure contains other cations, they will of course influence the stereochemical effect of the lone pair. Accordingly the s-p hybridization of the ns^2 electron pair is promoted by a low coordination number i.e. high bonding strength of thallium. Some oxygen-containing compounds of lead (6.2.2.) are treated as the Tl(I) salts in Table 6.2.1.

Table 6.2.1. Coordination number, structure type (or coordination polyhedron) and bond distances for some thallium(I) and rubidium oxygen compounds.

Compound	Coord. number	Structure type	Distances (Å) Tl-O and Rb-O	Remarks	Ref.
Tl ₂ O	3	anti-CdI ₂	2.52-2.53	active electron pair	63
	3	"	2.51-2.53		
Tl(I) ₃ Tl(III)O ₃	3	triangular pyram.	2.46-2.58	active electron pair	64
	3	" "	2.52-2.67	" " "	
	3+2	onesided coord.	2.40-2.73, 3.04(2x)	" " "	
Tl ₂ SO ₄	10	irregular	2.99-3.26		19
	9	"	2.85-3.21		
TlNO ₃	8		2.94-3.12		65
Tl ₃ PO ₄	3	triangular pyram.	2.53-2.55	active electron pair	66
Tl ₅ SbO ₅	3+1	one-sided coord.	2.47-2.74, 3.10	active electron pair	67
	3+1	" "	2.28-2.49, 3.33	" " "	
	3+2	" "	2.45-2.68, 2.98-3.16	" " "	
	3+1	" "	2.46-2.76, 2.88	" " "	
	2	" "	2.52(2x)	" " "	
	3	triangular pyram.	2.45-2.54	" " "	
TlSbO ₃	3	triangular pyram.	2.54(3x)	active electron pair	68
	3	" "	2.52(3x)	" " "	
Tl ₂ CO ₃	4+1+1	one-sided coord.	2.67-2.69, 3.24-3.36	active electron pair	69
	5+2	" "	2.68-2.82, 3.37(2x)	" " "	
Tl ₆ Si ₂ O ₇	3	triangular pyram.	2.41-2.52	active electron pair	70
	3	" "	2.38-2.81	" " "	
Tl ₂ SnO ₃	4	one-sided coord.	2.49-2.89	active electron pair	71
	3+3	octahedron, distorted	2.53-2.56, 3.19-3.22	" " "	
Tl ₃ BO ₃	3	triangular pyram.	2.48-2.54	active electron pair	72
Tl ₃ BO ₃	3	triangular pyram.	2.45-2.56	active electron pair	70
Tl ₂ TiO ₃	3+1	one-sided coord.	2.48-2.59, 3.13	active electron pair	62
	3+1		2.41-2.57, 3.22		
Tl ₂ Ti ₄ O ₉	10		2.79-3.44		73
	7		2.70-3.42		
TlVO ₃	10	irregular	2.88-3.42	isotypic to RbVO ₃	74
Tl ₂ CrO ₄	9	irregular coord.	2.70-3.36	isotypic to Rb ₂ CrO ₄	21
	9	" "	2.71-3.23		

Table 6.2.1. continued

Compound	Coord. number	Structure type	Distances (Å) Tl-O Rb-O	Remarks	Ref.
$\text{Tl}_2\text{Mo}_7\text{O}_{22}$	5+2		2.67-2.95, 3.26-3.32		75
TlNbB_2O_6	6	octahedron distorted	2.76-3.23		76
$\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$	6	octahedron	3.14(6x)	isotypic to $\text{Rb}_2\text{PbCu}(\text{NO}_2)_6$	77
Rb_2O	4	anti- CaF_2	2.92		78
Rb_2SO_4	10 9	irregular coord.	2.91-3.31 2.88-3.24	isotypic to Tl_2SO_4	18
$\text{RbH}_3(\text{SeO}_3)_2$	8	cube distorted	2.94-3.19		79
RbPO_3	6+1	octahedron distorted	2.95 (m.v for 6 atoms), 3.19		80
$(\text{RbPO}_3)_n$	7	unsymmetric	2.90-3.20		81
$\text{Rb}_6\text{Si}_{10}\text{O}_{23}$	7 7 8 7		3.02-3.12 3.02-3.30 3.07-3.28 2.95-3.19		82
Rb_2PbO_3	6	triangular prism	2.87-3.18		83
$\text{Rb}_2\text{In}_4\text{O}_7$	9		3.07(6x), 3.25(3x)		84
$\text{Rb}_2\text{Ge}_4\text{O}_9$	11		2.82-3.58		85
RbIO_3	12	cube octahedron	3.10-3.38		86
Rb_2TiO_3	5+2 7		2.89-3.06, 3.36(2x) 2.86-3.05		87
Rb_2CrO_4	10 9		3.15 (mean value) 3.21 (mean value)		20
$\text{Rb}_2\text{Cr}_2\text{O}_7$	8 9 8 9		2.86-3.28 2.89-3.24 2.87-3.09 2.90-3.31	$\text{P}\bar{1}$	88
$\text{Rb}_2\text{Cr}_2\text{O}_7$	8	irregular coord.	2.89-3.14	$\text{C}2/\text{c}$	89
$\text{Rb}_2\text{Cr}_2\text{O}_7$	8 8	irregular coord.	2.90-3.17 2.86-3.08	$\text{P}2_1/\text{n}$	90
$\text{Rb}_2\text{Cr}_3\text{O}_{10}$	11 10	irregular coord.	2.91-3.35 2.98-3.39		91
$\text{Rb}_2\text{Cr}_4\text{O}_{13}$	11 11	irregular coord.	2.88-3.47 2.89-3.35		92
$\text{RbTl}(\text{III})(\text{SO}_4)_2$	6	octahedron	2.98(6x)		93
$\text{RbVO}_2(\text{NO}_3)_3$	2+6+6	irregular coord.	2.93(2x), 3.18(6x), 3.29(6x)		94
$\text{RbBi}(\text{MoO}_4)_2$	8	irregular coord.	2.77-3.12		95
$\text{RbAlSi}_3\text{O}_8$	9		2.95-3.17		96
$\text{Rb}_2\text{TiGe}_3\text{O}_9$			2.84-3.69		85
$\text{RbFe}(\text{CrO}_4)_2$	10		2.89-3.17		97
$\text{RbNbO}(\text{SO}_4)_2$	8		2.90-3.19		98
$\text{Rb}_2\text{PbCu}(\text{NO}_2)_6$	6	octahedron, distorted	3.13-3.17		99

As seen even in these compounds the cation seems to make use of its inert electron pair when there are few oxygens to coordinate.

Table 6.2.2. The ratio O/Pb versus the presence of a stereochemical active electron pair.

Compound	Ratio: $\frac{O}{Pb}$	Remarks
PbO (yellow) ¹⁰⁰	1	active e ⁻ -pair
PbO (red) ¹⁰¹	1	"
Pb ₃ O ₄ ¹⁰²	1.33	" 2 Pb(II) 1 Pb(IV)
Pb ₂ O ₃ ¹⁰³	1.5	" 1 Pb(II) 1 Pb(IV)
Pb ₃ (PO ₄) ₂ ¹⁰⁴	2.67	no active e ⁻ -pair
PbSO ₄ ¹⁰⁵	4	"

A comparison between the shortest distances Tl-O and Rb-O, respectively, for the compounds given in Table 6.2.1, shows the difference 0.39 Å, between Tl-O 2.38 Å in Tl₆Si₂O₇ and Rb-O 2.77 Å in RbBi(MoO₄)₂. The shortest distance Tl-O reported is 2.28 Å for the compound Tl₅SbO₅, the standard deviation, 0.07 Å, about twice the values reported for the above-mentioned two salts.

6.3. Thallium(I) and Rubidium to sulphur

In the system thallium-sulphur the compounds Tl₂S, Tl₄S₃, TlS, TlS₂ and Tl₂S₅ are known. The substances TlS and Tl₄S₃ are double sulphides, T(I)Tl(III)S₂ and Tl₃(I)Tl(III)S₃ respectively. The two phases of Tl₂S₅, black and red in colour, have different crystal structures. As the black modification has a larger unit-cell than the red one it is assumed that the polysulphide ion S₅²⁻ has a trans-configuration in this compound.

The rubidium sulphides Rb_2S , Rb_2S_2 , Rb_2S_3 , Rb_2S_4 , Rb_2S_5 and Rb_2S_6 are identified. Only the structure of Rb_2S is known. It crystallizes in an anti- CaF_2 structure where the rubidium ion is tetrahedrally surrounded by four sulphur atoms.

In Tl_2S , Tl_2S_5 and TlAsS_2 the univalent thallium atom is 3-coordinated. The coordination polyhedron is a triangular pyramid. The inert pair of electrons is stereochemically active and occupies the fourth corner in the tetrahedral position in these compounds. In Tl_4S_3 the stereochemical effect of the $6s^2$ pair is not so clearly pronounced.

The shortest reported Tl-S distance of the compounds in Table 6.3.1 is 2.51 Å for Tl_2S , without standard deviation, however. In the compound Tl_4S_3 the shortest Tl-S distance is 2.90(4) Å. This distance is compared to the only reported Rb-S distance of 3.31 Å in Rb_2S which gives a difference of 0.41 Å.

Table 6.3.1. Coordination number, structure type (or coordination polyhedron) and bond distances for some thallium(I) and rubidium sulphur compounds.

Compound	Coord. number	Structure type	Distances (Å) Tl-S or Rb-S	Remarks	Ref.
Tl(III)Tl(I)S_2	8		3.33(8x)		106
Tl_2S	3	anti- CdI_2 , distorted	2.78-2.92	active electron pair	107
	3		3.14-3.28		
	3		2.78-3.23		
	3		2.66-2.68		
	3		2.51-2.70		
	3		2.51-2.70		
$\text{Tl(III)Tl(I)}_3\text{S}_3$	5	irregular coord.	2.94-3.36		108
	4	one-sided coord.	2.90-3.16		
	4		3.06-3.31		
Tl_2S_5	3+3	triangular pyramide	3.04-3.26, 3.43-3.49	active electron pair	109
	3+4		3.10-3.30, 3.35-3.47		
TlAsS_2	3		2.87-3.25		110
	3		2.84-3.0		

6.4. Thallium(I) and Rubidium to halogens, oxygen and sulphur

Only in one of the compounds given in Table 6.4.1, namely in Tl_3FCO_3 , the thallium atoms have a distinct stereochemically active electron pair. The environments of the three thallium(I) ions in Tl_3FCO_3 are nearly identical, each having four near and three more distant neighbours. The general geometry of these seven (5 oxygen and two fluorine atoms) atoms can be described as an one-capped octahedron (Fig. 6.4.1).

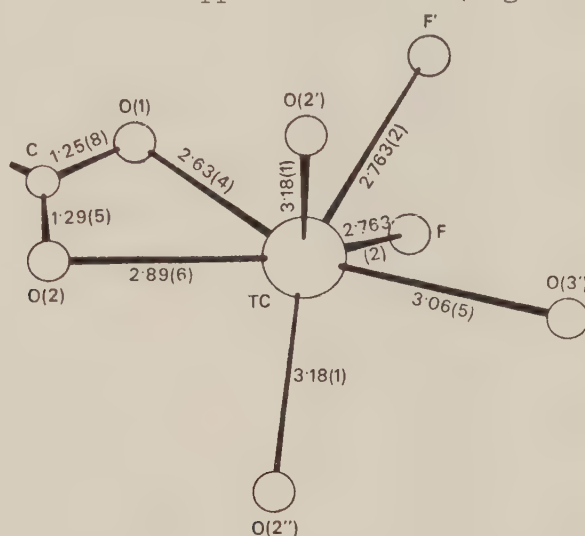


Fig. 6.4.1. Environment of one of the thallium atoms in Tl_3FCO_3 according to Alcock¹¹².

The three long Tl-O distances are to atoms forming one face of the octahedron, while the shortest distance (2.63 Å) is to the capping oxygen atom. According to Alcock, this is a very clear result of a distorted "inert" pair, in which the s^2 pair of the thallium atom has become non-symmetrical, probably by mixing with a p-orbital. This gives the thallium(I) ion a variable ionic radius, ranging from 1.23 to 1.78 Å, if the ionic radii for F^- and O^{2-} are assumed to be 1.36 and 1.40 Å, respectively.

In Table 6.4.1. a very short Rb-O distance, 2.78(4) Å, is reported for the compound $\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$.

Table 6.4.1. Coordination number, structure type (or coordination polyhedron) and bond distances for some thallium(I) and rubidium compounds.

Compound	Coord. number	Structure type	Bond distances	Remarks	Ref.
$\text{Tl}_2\text{S}_2\text{O}_3$	10	irregular coord.	$\text{Tl-O} = 3.07\text{-}3.46$ $\text{Tl-S} = 3.12\text{-}3.47$	$\text{S}_2\text{O}_3^{2-}$ disordered	4
	9		$\text{Tl-O} = 2.91\text{-}3.16$ $\text{Tl-S} = 3.20\text{-}3.29$		
Tl_3FCO_3	7	one-capped octahedron	$\text{Tl-F} = 2.74(2x)$ $\text{Tl-O} = 2.57\text{-}3.17$	active electron pair	112
	7		$\text{Tl-F} = 2.76(2x)$ $\text{Tl-O} = 2.63\text{-}3.18$		
	7		$\text{Tl-F} = 2.75(2x)$ $\text{Tl-O} = 2.64\text{-}3.19$		
$\text{Tl}_3[\text{Hg}(\text{SO}_4)_2] \cdot [\text{HgSO}_4\text{Cl}]$	10	irregular coord.	$\text{Tl-O} = 2.80\text{-}3.25$ (8 atoms) $\text{Tl-Cl} = 3.35$ $\text{Tl-O} = 3.45$ $\text{Tl-O} = 2.60\text{-}3.21$ (7 atoms)	Isotypic to corresponding Rb compound	2
	9	"	$\text{Tl-Cl} = 3.34$ $\text{Tl-O} = 3.40$ $\text{Tl-O} = 2.68\text{-}3.20$ (5 atoms)		
	10	" "	$\text{Tl-O} = 3.44\text{-}3.55$ (4 atoms) $\text{Tl-Cl} = 3.60$		
TlZnSO_4Cl	8+1	three-capped trigonal prism	$\text{Tl-O} = 2.89\text{-}3.16$ (5 atoms) $\text{Tl-Cl} = 3.21\text{-}3.29$ (3 atoms) $\text{Tl-O} = 3.48$	isotypic to RbZnSO_4Cl	3
$\text{Tl}_2[\text{Cu}(\text{SO}_3)_2]$	10	half a cube octahedron	$\text{Tl-O} = 2.82\text{-}3.04$ (6 atoms) $\text{Tl-S} = 3.21$ $\text{Tl-O} = 3.28\text{-}3.36$ (3 atoms)		113
RbClO_3	8		$\text{Rb-Cl} = 3.81(2x)$ $\text{Rb-O} = 3.53(6x)$		114
RbPO_2F_2	12		$\text{Rb-F} = 3.02\text{-}3.58$ (6 atoms) $\text{Rb-O} = 2.88\text{-}3.14$ (6 atoms)		115
$\text{Rb}_2(\text{As}_2\text{F}_{10}\text{O})\text{H}_2\text{O}$	13	irregular coord.	$\text{Rb-F} = 2.82\text{-}3.29$ (8 atoms) $\text{Rb-F} = 3.48\text{-}3.57$ (3 atoms) $\text{Rb-O} = 3.08\text{-}3.19$ (2 atoms)		116

Table 6.4.1 continued

Compound	Coord. number	Structure type	Bond distances	Remarks	Ref.
$\text{Rb}_3[\text{Hg}(\text{SO}_4)_2] \cdot [\text{HgSO}_4\text{Cl}]$	8+2		Rb-O = 2.91-3.08 (7 atoms)	isotypic to corresponding Tl compound	2
			Rb-Cl = 3.38		
			Rb-O = 3.39-3.43 (2 atoms)		
	9		Rb-O = 2.81-3.24 (8 atoms)		
			Rb-Cl = 3.32		
			Rb-O = 2.78-3.38 (7 atoms)		
	7+3		Rb-O = 3.49-3.52 (2 atoms)		
			Rb-Cl = 3.66		
RbZnSO_4Cl		three-capped trigonal prism	Rb-O = 2.90-3.11 (5 atoms)	isotypic to TlZnSO_4Cl	3
	8+1		Rb-Cl = 3.33-3.40 (3 atoms)		
			Rb-O = 3.69		
RbCrO_3Cl		irregular coord.	Rb-Cl = 3.42-3.55 (3 atoms)		17
	11		Rb-O = 2.94-3.15 (7 atoms)		
			Rb-O = 3.38		
$\alpha\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$	8	Cube	Rb-Cl = 3.38-3.57 (8 atoms)		117
$\beta\text{-RbMnCl}_3 \cdot 2\text{H}_2\text{O}$	8	Cube	Rb-Cl = 3.31-3.62 (8 atoms)		117
RbReO_3S			Rb-S = 3.58-3.61 (3 atoms)		118
	11		Rb-O = 2.87-3.25 (7 atoms)		
			Rb-O = 3.50		

7. A COMPARISON BETWEEN THE COORDINATION OF THALLIUM AND RUBIDIUM IN THE COMPOUNDS $M_3[Hg(SO_4)_2][HgSO_4Cl]$ AND $MZnSO_4Cl$, WHERE $M=Ti$ AND Rb , RESPECTIVELY

In the following description the oxygen and the chlorine atoms which are situated within a sphere of 3.0 Å and 3.4 Å, respectively from the thallium ion are regarded as the nearest neighbours. Corresponding values for the rubidium ion are about 0.02 Ångström units longer, cf. the values of Shannon & Prewitt in Table 5.1. Furthermore, a necessary assumption for the discussion is that a significant difference in distances between nearest and next nearest neighbours is available. According to Cruickshank¹¹⁹, the ratio $\frac{\Delta}{\sigma(\Delta)}$, where Δ stands for the difference in the distances and $\sigma(\Delta)$ for the standard deviation, is equal or greater than 3.3, the difference in the distances is considered to be significant. If the quotient $\frac{\Delta}{\sigma(\Delta)} \approx 2.5$, the difference is probably significant.

The $Tl(1)$ atom in $Tl_3[Hg(SO_4)_2][HgSO_4Cl]$ is surrounded by eight oxygen atoms at distances between 2.80 and 3.25 Å, and by one chlorine atom at 3.35 Å. No significant differences could be attributed to the $Tl-O$ distances outside 3.0 Å. (Fig. 7.2). A ninth oxygen atom is situated at a distance of 3.45 Å. The $Rb(1)$ atom in $Rb_3[Hg(SO_4)_2][HgSO_4Cl]$ is surrounded by seven oxygen atoms at distances between 2.91 and 3.08 Å and by one chlorine atom at 3.38 Å. Also in this case no significant differences were found. (Fig. 7.2). An eighth and a ninth oxygen atom are situated 3.39 and 3.43 Å apart, (Table 7.1):

Table 7.1. Selected distances (Å) with standard deviations in parentheses in the structures of $M_3[Hg(SO_4)_2][HgSO_4Cl]$, where M = Tl or Rb. Notations, cf. Fig. 7.1.

Distances	M = Tl	M = Rb
M(1)-O(3B)	2.80(3)	2.91(2)
M(1)-O(1C)	2.90(3)	2.97(2)
M(1)-O(2A)	2.96(3)	2.91(2)
M(1)-O(2B)	3.03(4)	3.08(3)
M(1)-O(1D)	3.03(3)	3.02(2)
M(1)-O(1A)	3.08(3)	3.05(2)
M(1)-O(3A)	3.14(4)	2.96(2)
M(1)-O(2D)	3.25(3)	3.43(2)
M(1)-Cl	3.35(1)	3.38(1)
M(1)-O(2C)	3.45(4)	3.39(3)
M(2)-O(3A)	2.60(4)	2.81(2)
M(2)-O(2A)	2.87(3)	3.06(2)
M(2)-O(2B)	2.94(4)	3.00(3)
M(2)-O(2C)	3.00(4)	2.86(3)
M(2)-O(1B)	3.09(3)	3.05(2)
M(2)-O(3C)	3.14(4)	3.03(2)
M(2)-O(3D)	3.21(4)	3.16(2)
M(2)-Cl	3.34(1)	3.32(1)
M(2)-O(2D)	3.40(3)	3.24(2)

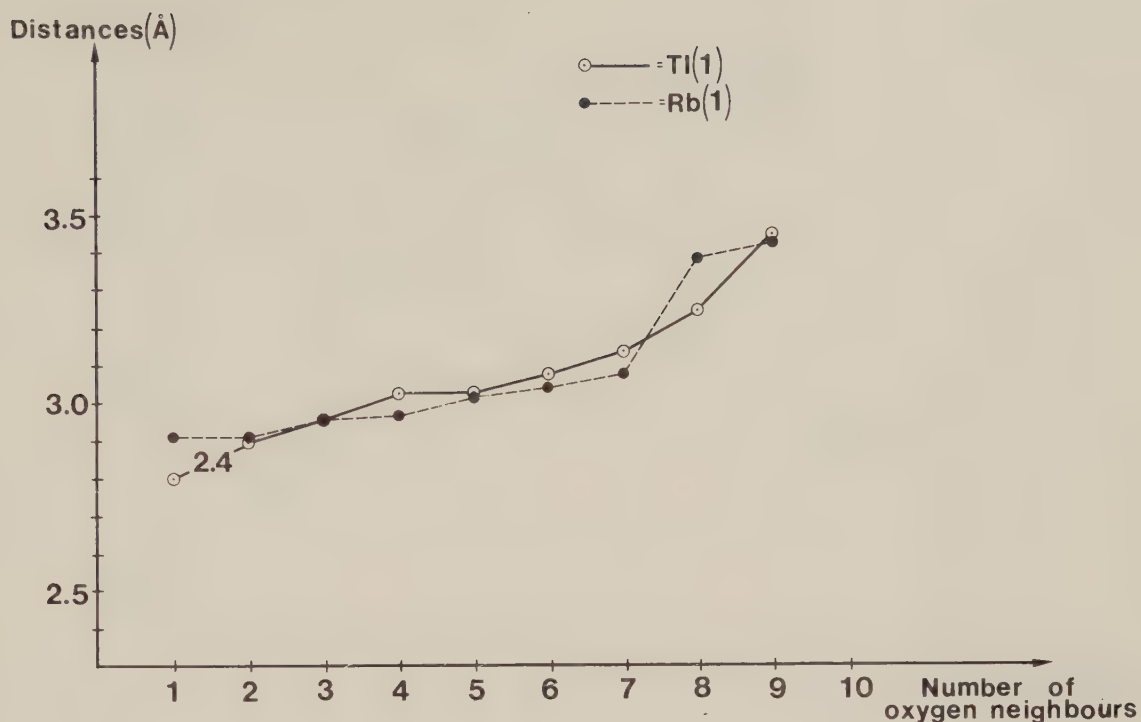


Fig. 7.2. The distance M-O as a function of the number of oxygen neighbours surrounding the metal atom. A value of the ratio $\frac{\Delta}{\sigma(\Delta)}$ is given.

Tl(2) in $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ has seven oxygen neighbours at distances between 2.60 and 3.21 Å and one chlorine atom at 3.34 Å. An eighth oxygen atom is situated at a distance of 3.40 Å. Rb(2) in the corresponding rubidium salt, is surrounded by six oxygen atoms at distances between 2.81 and 3.06 Å and by one chlorine atom at 3.32 Å. A seventh and an eighth oxygen atom are situated 3.16 and 3.24 Å apart. (Table 7.1). The same coordinations are valid for these atoms as stated for Tl(1) and Rb(1) above (Fig.7.3). The environments of the Tl(1) and Tl(2) atoms are shown in a stereo-view (Fig.7.1).

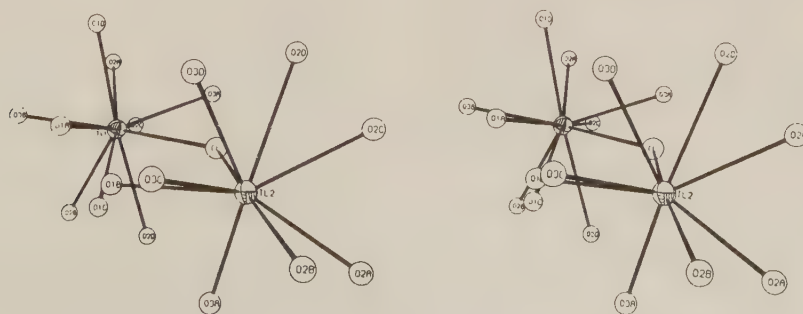


Fig. 7.1. Stereoscopic illustration showing the environments of the Tl(1) and Tl(2) atoms.

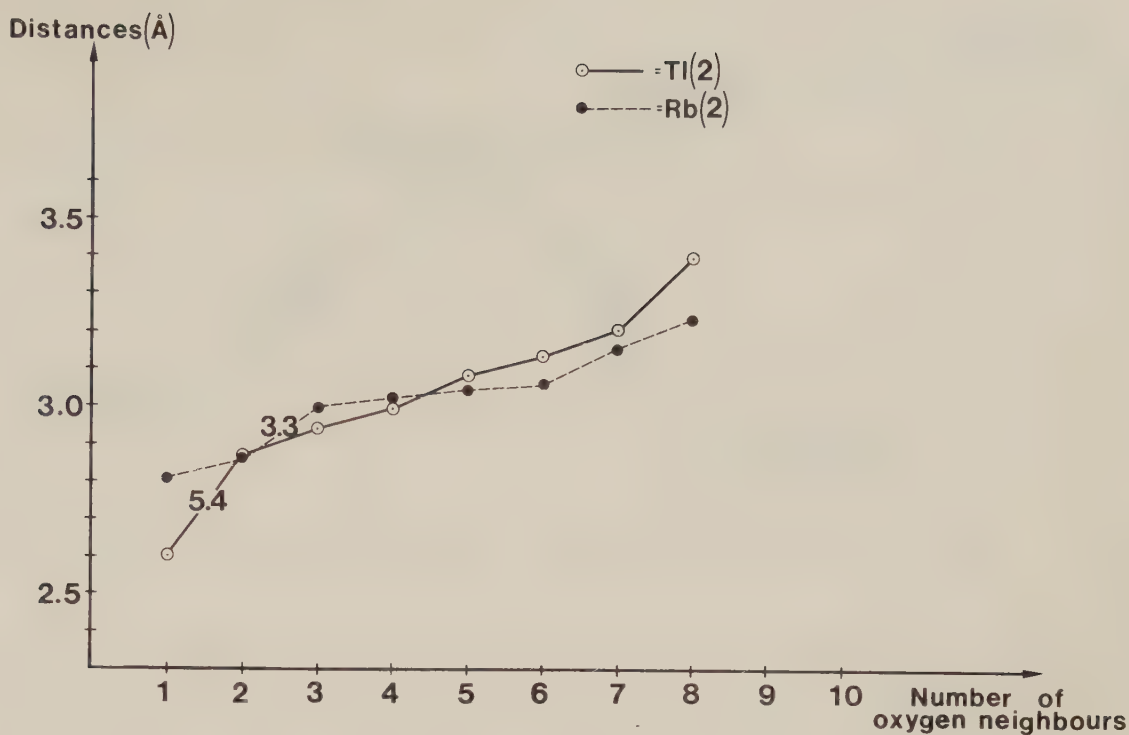


Fig. 7.3. The distance M-O as a function of the number of oxygen neighbours surrounding the metal atom. Two values of the ratio $\frac{\Delta}{\sigma(\Delta)}$ are given.

Nearest neighbours to Tl(3) and Rb(3) in the actual compounds are O(2B), O(1A) and O(3C) (Fig.7.4). The M-O distances are presented in Table 7.2.

Table 7.2. Distances M-O (Å) for the three nearest oxygen atoms in the structure of $M_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$.

	M = Tl	M = Rb
M(3)-O(2B)	2.68(4)	2.78(3)
M(3)-O(1A)	2.89(3)	2.96(2)
M(3)-O(3C)	2.95(4)	2.87(2)

The oxygen atoms define a plane and the thallium atom is displaced 0.05 Å out of this plane (Fig.7.4).

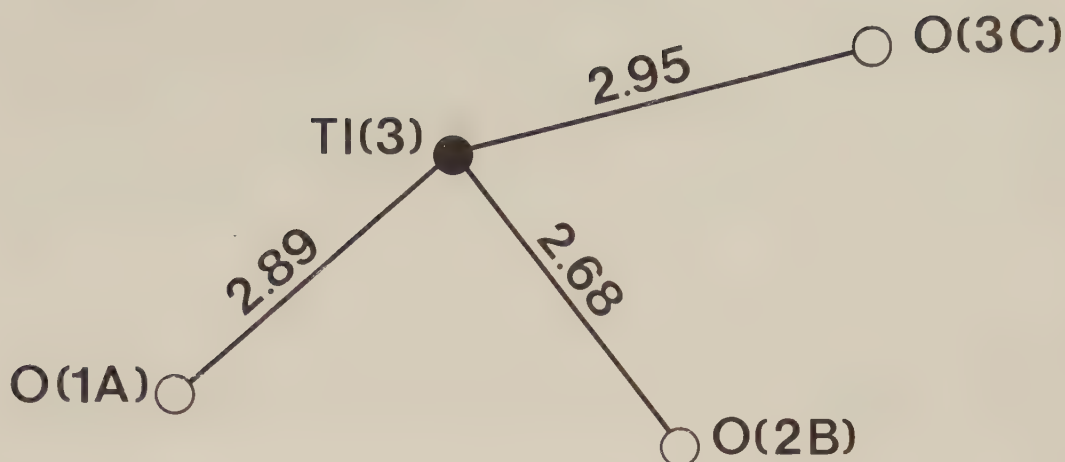


Fig. 7.4. The coordination Tl(3) to its nearest oxygen atoms.

Tl-O and Rb-O distances ≤ 3.6 Å with values of $\Delta/\sigma(\Delta)$ are shown in Fig. 7.5. As can be seen there is a very marked difference in the distances between the three nearest and the next nearest oxygen neighbours.

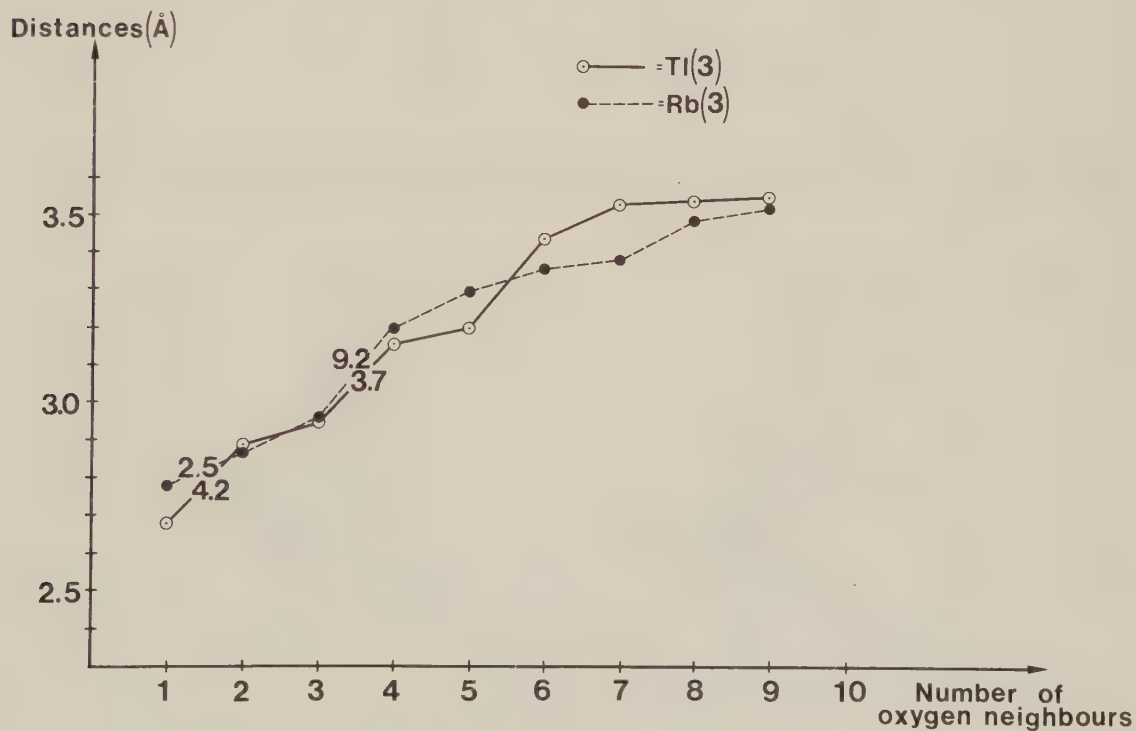


Fig. 7.5. The distance M-O as a function of the number of oxygen neighbours surrounding the metal atom. Some values of the ratio $\frac{\Delta}{\sigma(\Delta)}$ are given.

In the compound TlZnSO_4Cl the thallium atom has five close ligands, viz. two oxygen and three chlorine atoms. In the isotypic rubidium salt the rubidium atom has six nearest neighbours; three oxygen and three chlorine atoms. The distances are given in Table 7.3.

Table 7.3. Selected distances (Å) with standard deviations in parentheses in the structures of MZnSO_4Cl , where $\text{M} = \text{Tl}$ or Rb . Notations, cf. Fig. 7.6.

Distances	$\text{M} = \text{Tl}$	$\text{M} = \text{Rb}$
$\text{M}-\text{O}(3)$	2.89(1)	2.90(1)
$\text{M}-\text{O}(3)$	3.01(1)	2.94(1)
$\text{M}-\text{O}(4)$	3.18(1)	3.04(1)
$\text{M}-\text{Cl}$	3.206(4)	3.334(3)
$\text{M}-\text{Cl}$	3.275(3)	3.342(3)
$\text{M}-\text{Cl}$	3.293(4)	3.396(3)

The thallium atom is one-sidedly coordinated by the ligands (Fig.7.6).

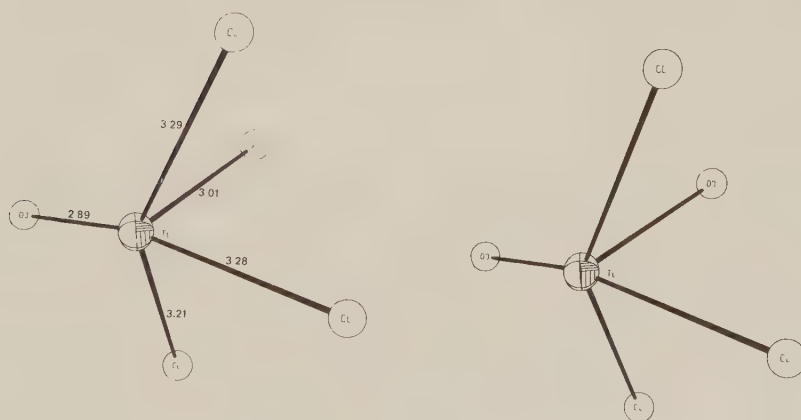


Fig. 7.6. Stereo view showing the environment of the Tl atom in TlZnSO_4Cl .

The one-sided coordination is not so pronounced for the rubidium atom because an additional oxygen atom is situated within the coordination sphere. Tl-O and Rb-O distances ≤ 3.7 Å with values of $\Delta/\sigma(\Delta)$ are given in Fig.7.7.

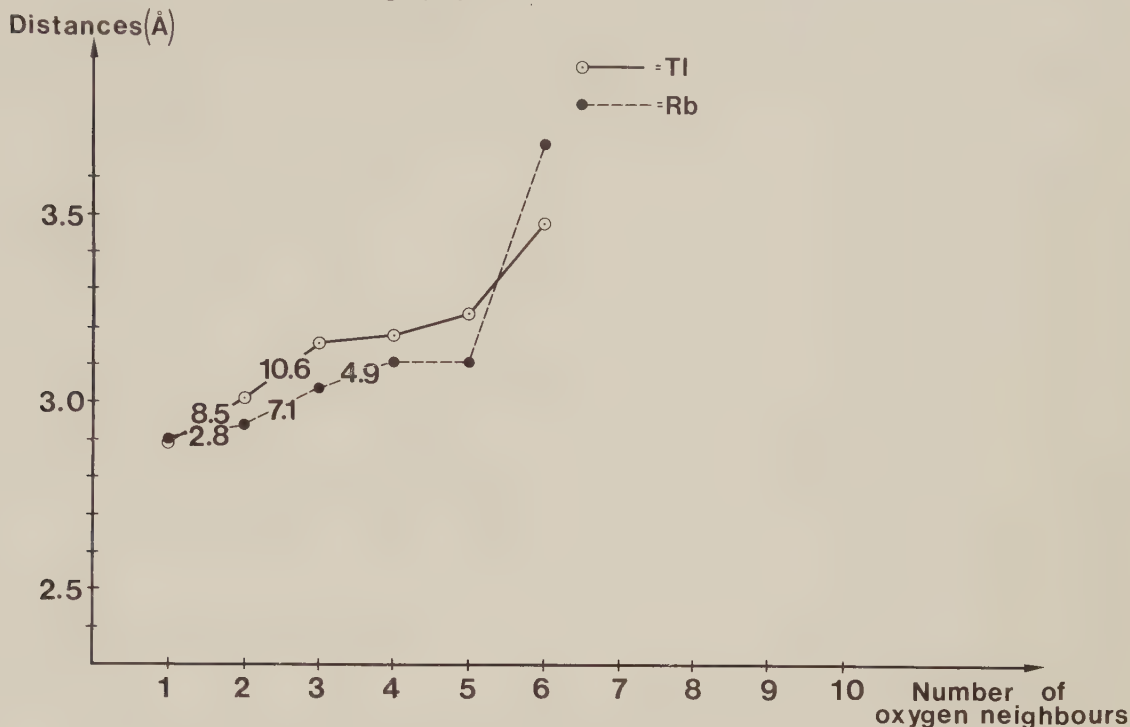


Fig. 7.7. The distance M-O as a function of the number of oxygen neighbours surrounding the metal atom. Some values of the ratio $\frac{\Delta}{\sigma(\Delta)}$ are given.

Regarding the coordination spheres around the thallium and rubidium ions in the structures now discussed, the following statements might be made:

- a) In isotypic thallium and rubidium compounds with asymmetric coordination polyhedra the shortest Tl-O distance is somewhat less than the corresponding Rb-O distance (cf. Fig.7.2, 7.3 and 7.5). Furthermore there is a larger difference between the M-O distances for the two nearest oxygen atoms bonded to Tl than in the case of Rb. Both these properties may be associated with a s-p hybridization of Tl^+ .

A symmetric coordination of Tl^+ is found in the structure of $\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$ (Table 6.2.1) where all oxygen atoms are situated at the same distance from Tl^+ . (Fig.7.8). This is a natural consequence of the symmetrical ligand field around Tl^+ in this case. The oxygen atoms are asymmetrically surrounding Rb^+ in the isotypic compound however.

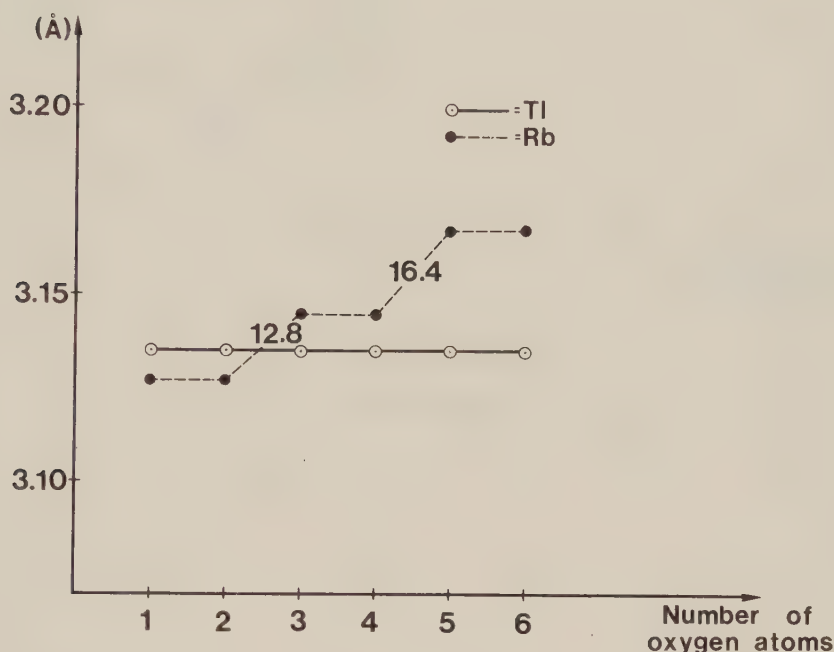


Fig. 7.8. The distance M-O as a function of the number of oxygen neighbours surrounding the metal atom. Some values of the ratio $\frac{\Delta}{\sigma(\Delta)}$ are given.

- b) In $\text{M}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ the $\text{Tl}(3)$ and $\text{Rb}(3)$ atoms are one-sidedly coordinated by three oxygen atoms at short distances (Fig.7.4, Table 7.2). A tetrahedral arrangement around the thallium atom with the inert pair of electrons in one of the corners would be possible. This assumption of a sp^3 hybridization of Tl^+ must be modified, however, as the distribution of the neighbours of Tl^+ is about the same as of Rb^+ and as Rb^+ has a noble gas shell. A very weak or a non-existing hybridization may be ascribed to Tl^+ . When Tl^+ and Rb^+ ions are surrounded by fluorine atoms, as in TlF and RbF , the same tendency as stated for the coordination of oxygen atoms is relevant (Fig.7.9 and 7.10).

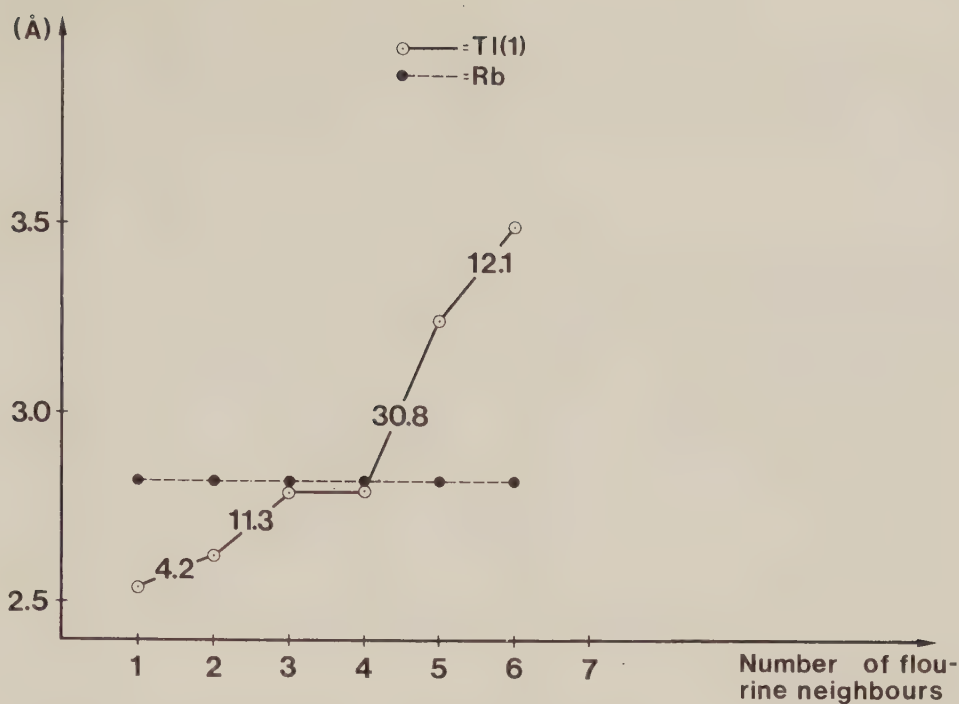


Fig. 7.9. The distance M-F as a function of the number of fluorine neighbours surrounding the metal atom. Some values of the ratio $\frac{\Delta}{\sigma(\Delta)}$ are given.

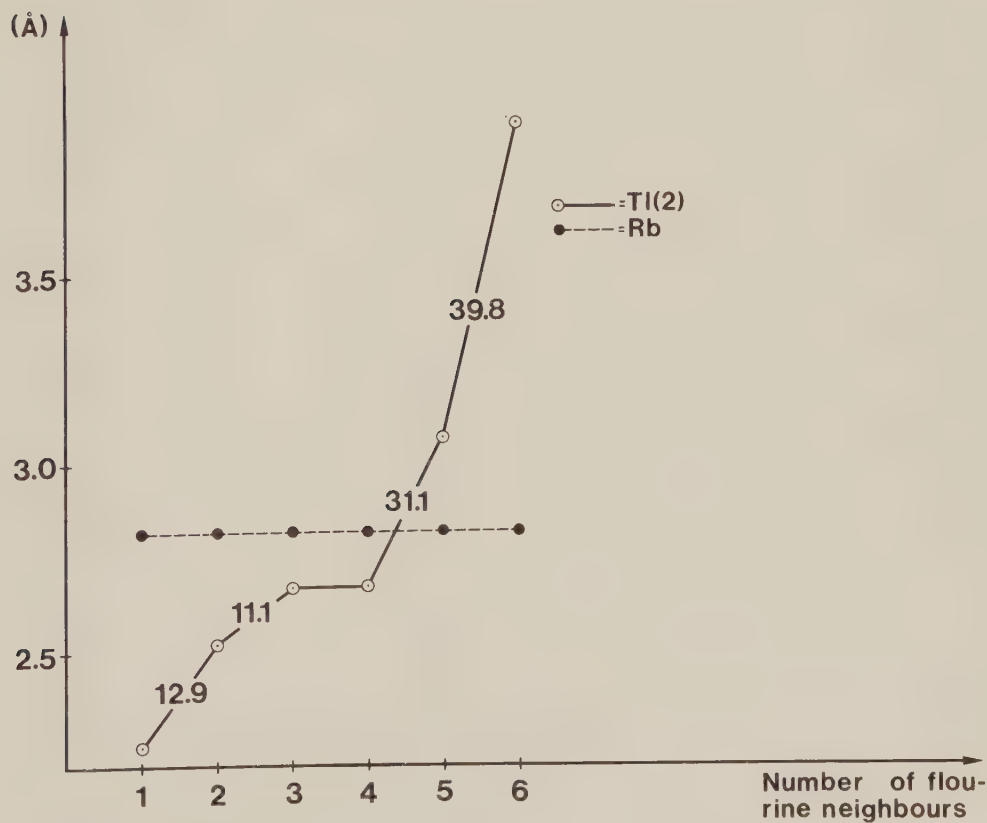


Fig. 7.10. The distance M-F as a function of the number of fluorine neighbours surrounding the metal atom. Some values of the ratio $\frac{\Delta}{\sigma(\Delta)}$ are given.

The "inert" pair of the Tl^+ ion is active in TlF which causes a more pronounced difference in the $Tl-F$ distances compared to the corresponding value in RbF .

Sleight & Jones have concluded that although Bi^{3+} and La^{3+} have essentially equal radii, the size of Bi^{3+} depends on the degree of stereochemical activity of the $6s^2$ pair. Table 7.4 shows a comparison of isotypic Bi^{3+} and La^{3+} compounds where the lone pair character of Bi^{3+} is constrained or dominant.

Table 7.4. Cell volumes ($\text{\AA}^3$) and their ratios of isotypic Bi^{3+} and La^{3+} compounds according to Sleight and Jones.

Lone pair character of Bi^{3+} constrained

Compound	Cell volume	Ratio
$BiLi(MoO_4)_2$	314.7	0.96
$LaLi(MoO_4)_2$	328.7	
$BiNa(MoO_4)_2$	320.5	0.97
$LaNa(MoO_4)_2$	332.1	
$BiOF$	87.6	0.90
$LaOF$	97.7	
$BiOCl$	110.7	0.95
$LaOCl$	116.8	
$BiOBr$	123.8	0.98
$LaOBr$	126.4	
$BiPO_4$	293.0	0.96
$LaPO_4$	304.7	

Lone pair character of Bi^{3+} dominant

Bi_2MoO_6	268.5(x8)	1.00
La_2MoO_6	267.3	
$BiFeO_3$	62.49(x6)	1.03
$LaFeO_3$	60.77(x4)	
$Bi_2Sn_2O_7$	1219.9(x8)	1.00

When Bi^{3+} is forced into high symmetry, the compound has a smaller unit-cell volume than the isotypic compound La^{3+} . When the lone-pair character is dominant, the structure of the Bi^{3+} compound is distorted and Bi^{3+} and La^{3+} salts have approximately equal cell volumes. If the same comparison is made for the isotypic Tl^+ and Rb^+ compounds studied in this paper, no observation as outlined by Sleight & Jones¹²⁰ can be made (Table 7.5).

Table 7.5. Cell volumes ($\text{\AA}^3$) and their ratios of isotypic Tl^+ and Rb^+ compounds.

Lone pair character of Tl^+ constrained.

Compound	Cell volume	Ratio
$\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$	713.9	0.99
$\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$	718.0	
TlZnSO_4Cl	561.0	0.97
RbZnSO_4Cl	577.4	
Tl_2SO_4	436	0.90
Rb_2SO_4	487	
Tl_2CrO_4	436	0.93
Rb_2CrO_4	469	
$\text{Tl}_2\text{PbCu}(\text{NO}_2)_6$	1240	1.00
$\text{Rb}_2\text{PbCu}(\text{NO}_2)_6$	1243	
TlBe_2F_5	473.4	0.98
RbBe_2F_5	484.3	

Lone pair character of Tl^+ dominant.

TlF	173.6	0.97
RbF	179.4	

It should be remarked that the comparison in Table 7.5 has been based on a small number of relevant compounds reported in this abstract. Further, the Bi^{3+} ion like the Tl^{+} ion has a varying degree of lone-pair character. Accordingly the distinction between constrained and dominant lone-pair character outlined in Table 7.4 is not easy to establish.

8. CONCLUDING REMARKS

I. In most of their oxygen and fluorine compounds In^+ , Sn^{2+} and Sb^{3+} have crystal structures which indicate the presence of a stereochemically active electron pair. In the crystal structures of oxygen and fluorine compounds of Tl^+ , Pb^{2+} and Bi^{3+} the influence of the inert electron pair seems to be more or less pronounced. Following Orgel³⁹ we may assume that this behaviour is due to a possible variation of hybridization of the 6s, 6p orbitals from absence to full activity.

In the Sb^{3+} compounds one may talk over the presence of an active electron pair in e.g. Sb_2O_3 (orth) or the absence of it in e.g. the SbCl_6^{3-} ion. The same conditions are valid for salts of Sn^{2+} . One may even locate the inert pair itself from the electrical field it gives which has excellently been shown by S. Andersson and coworkers.^{43,44}

In salts of Tl^+ , Pb^{2+} and Bi^{3+} the question is not if the inert electron pair is present or absent but to which degree it is present. The direction of the electrical field may be deduced from crystal structures but the distance of the electron pair from the central atom can not be inferred from measurements of this kind, because the stereochemical action of the pairs varies from compound to compound even if the ligands are the same.

We assume that the volume occupied by an inert electron pair in compounds of Tl^+ , Pb^{2+} and Bi^{3+} and the asphericity of the metal ion are proportional to the degree of hybridization of the 6s and 6p electrons. Consequently, if we start with a Tl^+ ion with an ionic radius of r in a symmetrical surrounding, the radius of Tl^+ in a compound with a large degree of sp hybridization would in some direction have a smaller value

than r . We take the minimum radius found in a Tl^+ compound as a crude measure of the sp hybridization. It may be mentioned that the degrees of hybridization of $TlI(\text{orth})$ and $TlI(\text{cube})$ have been estimated to 71 and 28 % respectively, whereas the corresponding shortest $Tl-I$ distances are 3.36 and 3.64 Å (cf. p. 30). Furthermore the compound $PbO(\text{orth})$ has a higher degree of hybridization than $PbO(\text{tetr})$ ¹²². The shortest $Pb-O$ distances are 2.21 and 2.31 Å, respectively. Table 8.1 shows shortest distances $M-X$, $M=Tl, Rb$ ($X = F, Cl, Br, I$), $M-O$ and $M-S$.

Table 8.1. Shortest distances d (Å) with $\sigma(d) \leq 0.04$ Å for the bondings $M-X$, $M = Tl, Rb$ ($X = F, Cl, Br, I$), $M-O$ and $M-S$. Radii of the anions are taken from Pauling²³ except for F and O , where the values are those given by Shannon and Prewitt (cf. Table 5.2). Calculated radii of the cations are also given.

Bonding	d	Ref.	Radius anion	Radius cation
$Tl-F$	2.25	38	1.29-1.33	0.96-0.92
$Tl-Cl$	3.15	32	1.81	1.34
$Tl-Br$	3.29	32	1.95	1.34
$Tl-I$	3.36	33	2.16	1.20
$Tl-O$	2.38	70	1.35-1.42	1.03-0.96
$Tl-S$	2.90	108	1.84	1.06
$Rb-F$	2.68	50	1.29-1.33	1.39-1.35
$Rb-Cl$	3.29	29	1.81	1.48
$Rb-Br$	3.43	29	1.95	1.48
$Rb-I$	3.63	58	2.16	1.47
$Rb-O$	2.78	2	1.35-1.42	1.43-1.36
$Rb-S$	3.31	111	1.84	1.47

The largest differences between the shortest bonds for corresponding Tl^+ and Rb^+ salts occur for the ligands F-O, S-I, cf. Fig.8.1 where cation radius is plotted against electronegativity of the anion atom.

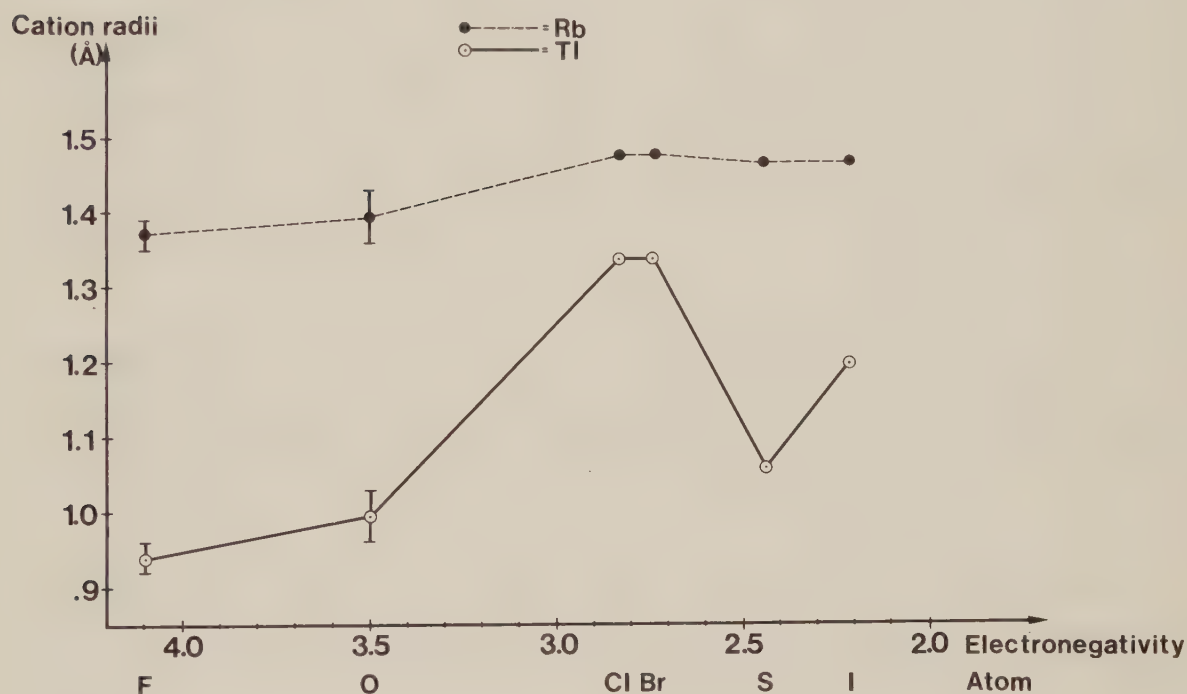


Fig. 8.1. Cation radius plotted against electronegativity of anion atom in some compounds of Tl and Rb (cf. Table 8.1). Values of electronegativity are according to Allred-Rochow¹²¹.

The peak in the Tl^+ curve may be explained by the Tl atoms being ionic in $\text{Tl}_6\text{Si}_2\text{O}_7$ and TlF but having a certain degree of sp hybridization, whereas the Tl^+ ions are spherically symmetric in TlCl and TlBr . Finally there may be some other kind of more covalent sp hybridization in Tl_4S_3 and TlI . Generally the degree of the sp hybridization of Tl^+ is only dependent on the ligand field.

II. The present investigation was started to compare bond distances in rubidium and thallium(I) compounds as Rb^+ and Tl^+ approximately have the same ionic radii. Rb^+ has a noble gas electron shell and Tl^+ has stereochemically active electron pairs to various extents in its compounds.

Isotypic compounds of Rb^+ and Tl^+ may be used to study the influence of the crystal field on the sp hybridization of Tl^+ . To make proper use of such comparisons it must, however, be ascertained that the Rb^+ ion is not polarized by the anions as Cs^+ is in Cs_2O , a structure closely related to that of Tl_2O .

Suitable pairs for comparison are $\text{RbZnSO}_4\text{Cl}/\text{TlZnSO}_4\text{Cl}$ and $\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]/\text{Tl}_3[(\text{Hg}(\text{SO}_4)_2)[\text{HgSO}_4\text{Cl}]$, both with irregular coordinations around Rb^+ and Tl^+ , cf. Table 8.2.

Table 8.2. Shortest distance d (Å) with $\sigma(d) \leq 0.04$ Å for the bonding M-O in the structures of $\text{M}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ and MZnSO_4Cl , $\text{M} = \text{Tl}^+$ or Rb^+ . The ionic radii of the oxygen atom are those given by Shannon and Prewitt (cf. Table 5.2).

Bonding	d	Ref	Radius Tl^+ or Rb^+ ion
$\text{Tl}(1)\text{-O}$	2.80	2	1.45-1.38
$\text{Tl}(2)\text{-O}$	2.60	2	1.25-1.18
$\text{Tl}(3)\text{-O}$	2.68	2	1.33-1.26
Tl-O	2.89	3	1.54-1.47
$\text{Rb}(1)\text{-O}$	2.91	2	1.56-1.49
$\text{Rb}(2)\text{-O}$	2.81	2	1.46-1.39
$\text{Rb}(3)\text{-O}$	2.78	2	1.43-1.36
Rb-O	2.90	3	1.55-1.48

In the pair $\text{TlZnSO}_4\text{Cl}/\text{RbZnSO}_4\text{Cl}$ there is no difference between the shortest Tl-O (2.89 Å) and Rb-O (2.90 Å) distances. Tl^+ may be assumed to be as spherical as Rb^+ .

In the $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]/\text{Rb}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$ pair the $\text{Tl}(2)\text{-O}$ distance (Table 8.2) is significantly shorter than the $\text{Rb}(2)\text{-O}$ distance, whereas the $\text{Tl}(1)\text{-O}$ and $\text{Tl}(3)\text{-O}$ distances are the same as the corresponding Rb-O distances within the limits of error. Some more general conclusions may be drawn from these examples.

- (i) The presence of an "one-sided" coordination of Tl^+ in a thallium-compound does not necessarily imply that Tl^+ is sp hybridized to a large extent since almost exactly the same coordination and distances may be found in an isotypic Rb compound cf. the pairs of compounds just discussed. Analogous examples are BiOCl and LaOCl (Table 7.4) and also red PbO for which a relatively low degree of sp hybridization is estimated.
- (ii) On the other hand the fact that Rb^+ and Tl^+ compounds are isotypic does not exclude that the Tl^+ atoms are partially sp hybridized. Small shifts less than 0.5 Å of the positions of the metal atoms in two corresponding compounds may lead to different metal-ligand coordinations.
- (iii) Tl^+ ions located at different crystallographic point positions in the same unit cell may have different degrees of hybridization. This observation is consistent with the assumption that the ligand field determines the hybridization, cf. TlF^{38} ,
 $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]^2$.

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10. REFERENCES

1. Bosson, B., Acta Chem. Scand. 27 (1973) 2230.
2. Bosson, B., Acta Chem. Scand. A30 (1976) 241.
3. Bosson, B., Acta Cryst. B32 (1976) 2044.
4. Andersson, J.-E. and Bosson, B., Acta Cryst. B32 (1976) 2225.
5. Luzhnaya, N.P. and Vereshchetina, I.P.,
Izvest. Sektora Fiz.-Khim. Anal., 27 (1956) 285; from
Chem. Abstr., 50 (1956) 15195.
6. Sil'nicenko, V.G., Uchenye Zapiski Moskov.
Oblast. Pedagog. Inst. 84 (1959) 119; from Chem. Abstr. 56
(1962) 4349.
7. McGinnety, J.A., Acta Cryst. B28 (1972) 2845.
8. International Tables for X-Ray Crystallography, Kynoch Press,
Birmingham 1962, vol III.
9. Cromer, D.T. and Libermann, D., J. Chem. Phys. 53 (1970) 1891.
10. Cromer, D.T. and Mann, J.B., Acta Cryst. A24 (1968) 321.
11. Doyle, P.A. and Turner, P.S., Acta Cryst. A24 (1968) 390.
12. Björnlund, G., Acta Chem. Scand. A28 (1974) 169.
13. Aurivillius, K. and Stålhandske, C. Z. Kristallogr. 144 (1976) 1.
14. Templeton, L.K., Templeton, D.H. and Zalkin, A.,
Acta Cryst. 17 (1964) 933.
15. Stålhandske, C., To be published.
16. Wells, Inorg. Struct. Chem. (1975) 402.
17. Foster, J.J. and Sterns, M., J. Cryst. Mol. Struct. 4 (1974) 149.
18. Nord, A.G., Acta Cryst. B30 (1974) 1640.
19. Pannetier, G. and Gaultier, M., C.R. Acad. Sci. Paris 263 (1966) 132.
20. Smith, H.W. and Colby, M.Y., Z. Kristallogr. 102 (1940) 90.
21. Carter, R.L. and Margulis, T.N., J. Solid State Chem. 5 (1972) 75.
22. Goldschmidt, V.M., Skr. norske Vidensk. Akad. Oslo, Math.-Nat.
K1., 2 (1926).

23. Pauling, L., Nature of the Chemical Bond, 3rd edn., Cornell University Press. Ithaca. New York. 1960.
24. Ladd, M.F.C., Theoret. Chim. Acta 12 (1968) 333.
25. Shannon, R.D. and Prewitt, C.T., Acta Cryst. B25 (1969) 925.
26. Shannon, R.D., Acta Cryst. A32 (1976) 751.
27. Fumi, F.G. and Tosi, M.P., J. Phys. Chem. Solids. 25 (1964) 31.
28. Pauling, L., J. Am. Chem. Soc. 49 (1927) 765.
29. Wyckoff, R.W.G., Crystal Structures vol 1. Interscience 1963.
30. Ketelaar, J.A.A., Z. Kristallogr. 92 (1935) 30.
31. Pistorius, C.W.F.T. and Clark, J.B., Phys. Rev., 173 (1968) 692.
32. Schulz, L.G., Acta Cryst. 4 (1951) 487.
33. Helmholtz, L., Z. Kristallogr. 95 (1936) 129.
34. Dunitz, J.D. and Orgel, L.E., Advances Inorg. Chem. Radiochem., 2 (1960) 43.
35. Schob, O. and Parthé, E., Acta Cryst. 19 (1965) 214.
36. Bovin, J.-O. and Andersson, S., J. Solid State Chem. 20 (1977) 127.
37. Piermarini, A.J. and Weir, C.E., J. Chem. Phys. 37 (1962) 1887.
38. Alcock, N.W., J.C.S. Dalton Trans. 17 (1974) 1907.
39. Orgel, L.E., J. Chem. Soc. (1959) 3815.
40. Boudreaux, E.A., Coord. Chem. Rev., 2 (1967) 117.
41. Hafner, S., J. Phys. Chem. Solids, 27 (1966) 1881.
42. Shannon, R.D. and Gummerman, P.S., J. Inorg. Nucl. Chem. 38 (1976) 699.
43. Åström, A. Thesis. University of Lund. (1972). Lund. Sweden.
44. Andersson, S. and Åström, A. NBS Special publication 354, Solid State Chemistry, Proceeding of 5th Materials Research Symposium, issued July 1972.
45. Le Fur, Y., Acta Cryst. B28 (1972) 1159.
46. Thiele, G. and Rink, W., Z. Anorg. Allg. Chem. 414 (1975) 231.

47. Hazell, A.C., J. Chem. Soc. (1963) 3459.
48. Brodersen, K., Thiele, G. and Görz, G., Z. Anorg. Allg. Chem. 401 (1973) 217.
49. Clark, M.J.R. and Lynton, H., Can. J. Chem. 47 (1969) 2579.
50. Hebecker, Ch., Z. Anorg. Allg. Chem. 412 (1975) 37.
51. Ilyukhin, V.V. and Belov, N.V. Doklady Akad. Nauk. S.S.S.R. 140 (1961) 1066.
52. Mustafaev, N.V., Ilyukhin, V.V. and Belov, N.V. Kristallografiya 10 (1965) 805.
53. Burns, J.H., Levy, H.A. and Lewin Keller, O., Acta Cryst. B24 (1968) 1675.
54. Jacoboni, C. and De Pape, R., Acta Cryst. B30 (1974) 2688.
55. Vicat, J., Tran Qui, D. and Aléonard, S., Acta Cryst. B32 (1976) 1356.
56. Aléonard, S. and Pouzet, C., J. Appl. Cryst. 1 (1968) 113.
57. Seifert, H.J. and Fink, H., Rev. Chim. Min. 12 (1975) 466.
58. Geller, S., Science, 157 (1967) 310.
59. Bovin, J.-O., Thesis. Lund 1975.
60. Gillespie, R.J. (1972) Molecular Geometry. London: van Nostrand-Reinhold.
61. Bovin, J.-O., Acta Cryst. B32 (1976) 1771.
62. Verbaere, A., Dion, M. and Tournoux, M., J. Solid State Chem. 11 (1974) 60.
63. Sabrowsky, H., Z. Anorg. Allg. Chem. 381 (1971) 266.
64. Marchand, R. and Tournoux, M., C.R. Akad. Sci. Paris 277 (1973) 863.
65. Fraser, W.L., Kennedy, W.S. and Snow, M.R. Acta Cryst. B31 (1975) 365.
66. Ganne, M. and Tournoux, M., C.R. Akad. Sci. Paris 276 (1973) 1755.
67. Bouchama, M. and Tournoux, M., Rev. Chim. Min. 12 (1975) 93.

68. Bouchama, M. and Tournoux, M., Rev. Chim. Min. 12 (1975) 80.
69. Marchand, R., Piffard, Y. and Tournoux, M.,
Can. J. Chem. 53 (1975) 2454.
70. Marchand, R., Piffard, Y. and Tournoux, M., Rev. Chim. Min. 12
(1975) 210.
71. Verbaere, A., Dion, M. and Tournoux, M., J. Solid State Chem. 11
(1974) 184.
72. Marchand, R., Piffard, Y. and Tournoux, M., C.R. Acad. Sci.
Paris 276 (1973) 177.
73. Verbaere, A. and Tournoux, M., Bull. Soc. Chim. Fran. 4 (1973) 1237.
74. Ganne, M., Piffard, M. and Tournoux, M., Can. J. Chem. 52
(1974) 3539.
75. Tolédano, P., Touboul, M. and Herpin, P.,
Acta Cryst. B32 (1976) 1859.
76. Gasperin, M., Acta Cryst. B30 (1974) 1181.
77. Takagi, S. and Joesten, D.J., Acta Cryst. B32 (1976) 326.
78. Helms, A. and Klemm, W., Z. Anorg. Allg. Chem. 242 (1939) 33.
79. Tellgren, R., Ahmad, D. and Liminga, R., J. Solid State Chem. 6
(1973) 250.
80. Cruickshank, D.W.J., Acta Cryst. 17 (1964) 681.
81. Corbridge, D.E.C., Acta Cryst. 2 (1956) 308.
82. Schichl, H., Völlenkne, H. and Wittman, A., Monatsh. Chem. 104
(1973) 854.
83. Seeger, K. and Hoppe, R., Z. Anorg. Allg. Chem. 375 (1970) 255.
84. Fink, D. and Hoppe, R., Z. Anorg. Allg. Chem. 409 (1974) 97.
85. Goreaud, M. and Raveau, B., Acta Cryst. B32 (1976) 1536.
86. Alcock, N.W., Acta Cryst. B28 (1972) 2783.
87. Schartau, W. and Hoppe, R., Z. Anorg. Allg. Chem. 408 (1974) 60.
88. Panagiotopoulos, N. Ch. and Brown, I.D., Can. J. Chem. 48 (1970) 537.

89. Löfgren, P. and Waltersson, K., Acta Chem. Scand. 25 (1971) 35.
90. Löfgren, P., Acta Chem. Scand. 25 (1971) 46.
91. Löfgren, P., Chemica Scripta, 5 (1974) 91.
92. Löfgren, P., Acta Cryst. B29 (1973) 2141.
93. Pannetier, G., Manoli, J.-M. and Herpin, P., Bull. Soc. Chim. Fr., (1972) 485.
94. Barclay, G.A., Sabine, T.M. and Taylor, J.C., Acta Cryst. 19 (1965) 205.
95. Klevtsova, R.F., Solofoeva, L.P. and Vinokurov, V.A., Kristallografiya, 20 (1975) 270.
96. Gasperin, M., Acta Cryst. B27 (1971) 854.
97. Bonnin, A., Hardy, A. and Garnier, E., C.R. Acad. Sci. Paris 276 (1973) 1381.
98. Kuznetsov, V. Ya. et al. Izv. Akad. Nauk S.S.S.R. 10 (1974) 2167.
99. Takagi, S. et al., J. Am. Chem. Soc. 97 (1975) 444.
100. Kay, M.J., Acta Cryst. 14 (1961) 80.
101. Leciejewicz, J., Acta Cryst. 14 (1961) 1304.
102. Leciejewics, J., Z. Anorg. Allg. Chem. 336 (1965) 104.
103. Bouvaist, J. and Weigel, D., Acta Cryst. A26 (1970) 501.
104. Keppler, U., Z. Kristallogr. 132 (1970) 228.
105. Sahl, K., Beitr. Mineral. Petrog. 9 (1963) 111.
106. Scatturin, V. and Frasson, E., Ric. Sci. 26 (1956) 3382.
107. Man, L.I., Sov. Phys. Cryst. 15 (1970) 399.
108. Leclerc, B. and Bailly, M., Acta Cryst. B29 (1973) 2334.
109. Leclerc, B. and Kabré, T.S., Acta Cryst. B31 (1975) 1675.
110. Zemann, A. and Zemann, J., Acta Cryst. 12 (1959) 1002.
111. May, K., Z. Kristallogr. 94A (1936) 412.
112. Alcock, N.W., Acta Cryst. B29 (1973) 498.
113. Hjertén, I. and Nyberg, B., Acta Chem. Scand. 27 (1973) 345.

114. Brunton, G., Mat. Res. Bull. 8 (1973) 791.
115. Granier, W., Durand, J., Cot, L. and Galigné, J.L.,
Acta Cryst. B31 (1975) 2506.
116. Hause, W., Acta Cryst. B30 (1974) 1722.
117. Jensen, S.J., Acta Chem. Scand. 21 (1967) 889.
118. Krebs, B. and Kindler, E., Z. Anorg. Allg. Chem. 368 (1969) 293.
119. Cruickshank, D.W.J. and Robertson, A.P., Acta Cryst. 6 (1953) 698.
120. Sleight, A.W. and Jones, G. Acta Cryst. B31 (1975) 2748.
121. Allred, A.L. and Rochow, E.G., J. Inorg. Nucl. Chem. 5 (1958) 264.
122. Orgel, L.E., Molecular Physics 1 (1958) 322.



